

New theory of the γ - α phase transition in Ce: quadrupolar ordering

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(February 1, 2008)

We present a theoretical model of the “isostructural” γ - α phase transition in Ce which is based on quadrupolar interactions due to coupled charge density fluctuations of $4f$ electrons and of conduction electrons. Conduction electrons are treated in tight-binding approximation. The γ - α transition is described as an orientational ordering of quadrupolar electronic densities in a $Pa\bar{3}$ structure. The quadrupolar order of the conduction electron densities is complementary to the quadrupolar order of $4f$ electron densities. The inclusion of conduction electrons leads to an increase of the lattice contraction at the γ - α transition in comparison to the sole effect of $4f$ electrons. We calculate the Bragg scattering law and suggest synchrotron radiation experiments in order to check the $Pa\bar{3}$ structure. The theory is capable of accounting for transitions to phases of non-cubic symmetry, but it is not sufficient to describe the magnetic phenomena which we ascribe to the Kondo mechanism. We also present a microscopic derivation of multipolar interactions and discuss the crystal field of γ -Ce.

I. INTRODUCTION

The understanding of the nature of the α phase and the apparently isostructural transition between the cubic γ - and α - phases in cerium is a long-standing problem [1,2]. Numerous experimental data present an outstanding challenge for the explanation by theoretical models [3–11]. The most important question to be answered by theory is to find the driving force of the “isostructural” γ - α transition and to explain also the existence of the other non-cubic phases of Ce.

The theory should also describe the change of magnetic properties of Ce at the γ - α transition [12,1] which are reminiscent of an insulator-metal transition of $4f$ electrons [3]. Recently the Mott transition has been reconsidered by several authors using electronic band structure calculations with thermodynamic extensions [4–6] (see for a review Ref. [7]). There, the α phase is described as a regular band state formed by $6s$, $5d$ and $4f$ electronic states while in γ -Ce different degrees of localization of $4f$ states are suggested and investigated. Two face centered cubic (fcc) phases of cerium are attributed to two local minima of free energy which develop for the same crystal structure ($Fm\bar{3}m$).

Assuming the localized nature of the $4f$ electrons throughout the γ - α phase transition, one can understand the magnetic properties on the basis of two principles. These are the singlet ground state of one $4f$ electron and the energy gap (characterized by the Kondo temperature T_K) separating the ground state from a manifold of excited magnetic states. So far these properties have been treated [10,11] on the basis of the Anderson impurity Hamiltonian [13] which implies an antiferromagnetic Kondo spin interaction. In order to describe the volume contraction [1] at the γ - α transition, the theoret-

ical models [8,9,7] exploit the volume dependence of the Kondo temperature. Such a “volume collapse” leads to a phase instability without symmetry change and is interpreted as an isostructural transition. However within the Kondo theory scenario, the existence of the other, non-cubic phases of Ce, remains unexplained. In the last few years the validity of this approach has been questioned by photoemission spectroscopy experiments [14–18] where the predicted temperature dependence of the intensity of the Kondo resonance at the Fermi level has not been observed. Recently it has appeared that the Kondo volume collapse model can not be applied to YbInCu₄ [19] which exhibits a 0.5% volume expansion during another isostructural phase transition [20] though Yb is the f-hole analogue of Ce. In addition, taking into account the thermal expansion of YbInCu₄ above the phase transition temperature $T = 42$ K one concludes that the Kondo temperature is not a unique function of cell volume [19].

An alternative theoretical model of the γ - α transition has been recently proposed by the present authors [21]. The theory is capable of accounting for transitions to phases of non-cubic symmetry. The quantum mechanical electric quadrupole interaction between $4f$ electrons on the fcc lattice is proposed as the driving mechanism of a phase transition. The γ -phase is characterized by the absence of spatial orientational order of the quadrupolar densities, the space group is $Fm\bar{3}m$. In the α -phase the quadrupolar densities order in a $Pa\bar{3}$ structure. Notice that this change from $Fm\bar{3}m$ to $Pa\bar{3}$ conserves the fcc structure of the atomic center of mass points and is solely due to orientational order of the quadrupoles. This phase transition is accompanied by a contraction of the fcc lattice, however the theoretical estimation of these effects in [21] (in the following we will denote this reference by I), is about an order of magnitude smaller than the

experimental result [1]. In addition the treatment of I does not indicate the existence of a critical end point of the phase separation line ($\gamma - \alpha$) in the $P - T$ (pressure-temperature) phase diagram.

In the present paper, we will extend the theoretical model of I by taking into account the polarization of $(6s5d)^3$ conduction band electrons. The polarization can be considered as a screening process of the quadrupolar density orientations of the $4f$ electrons and results in turn in a complementary ordered $Pa\bar{3}$ structure build up from conduction electron quadrupolar densities. The conduction electrons will be described within the formalism of tight binding approximation.

The paper comprises the following sections. We start (Sect. 2) with reconsidering $4f$ electrons and extending the treatment of I by taking into account the radial dependence of the $4f$ electron density. Next in section 3 we describe the conduction electrons in second quantization with basis functions in tight-binding approximation. We derive the multipolar interactions among conduction electrons as well as interactions with $4f$ electrons. In considering conduction electrons we have to distinguish between on- site and inter- site interactions. Section 4 is devoted to a study of the crystal field which acts on the individual $4f$ electron. It is found that the refinement by the radial density dependence of $4f$ electrons does not improve but rather spoils the agreement between experiment and theory. On the other hand the inclusion of conduction electrons improves in turn the situation. In Sect. 5 we study the quadrupolar ordering of the coupled system of $4f$ electrons and conduction electrons. We conclude that a state of lower free energy (in comparison with the disordered state) can be achieved by a complementary ordering of $4f$ electron and conduction electron quadrupolar densities. On a same atomic lattice site, high charge density regions of the $4f$ electron correspond to low charge density of the conduction electrons and vice versa. Finally we present numerical estimates that the inclusion of the conduction electron quadrupolar order improves the magnitude of the lattice contraction at the $Fm\bar{3}m \rightarrow Pa\bar{3}$ transition. In order to propose an unambiguous experimental proof of the present theoretical model, we calculate the Bragg scattering law and suggest synchrotron radiation experiments for the $Pa\bar{3}$ structure (These calculations will be presented in the full original version to be published in Eur. Phys. J. B, 2000). In Sect. 6 (Discussion) we recall the salient features of the present theory and situate it with respect to the conventional approaches that are based on the Kondo theory concepts. While we do not adopt the Kondo volume collapse models, we discuss the relevance of the Friedel-Anderson hybridization mechanism for the explanation of the magnetic anomalies in Ce and suggest a link with our theory of the electronic charge degrees of freedom driven structural phase transition.

II. RADIAL DEPENDENCE OF $4f$ ELECTRONS

In our previous paper [21] the quadrupolar coupling between $4f$ electrons has been calculated by assuming that the electron on each lattice site \vec{n} is localized on a sphere with a fixed radius $r_f = 1.378$ a.u. Here we want to extend the previous calculation by taking into account the radial dependence of the $4f$ electron wave functions. Such an extension is necessary if we want to study the interaction with the conduction electrons (see next sections). Furthermore it is useful in assessing the validity of our previous calculations.

We consider a face centered cubic crystal of N Ce atoms. Each atomic core possesses one $4f$ electron. In the γ -phase the $4f$ electron densities are orientationally disordered. The space group of the crystal is $Fm\bar{3}m$. The Coulomb interaction between two $4f$ electrons (charge $|e|=1$) at positions $\vec{R}(\vec{n})$ and $\vec{R}'(\vec{n}')$ near the lattice sites \vec{n} and \vec{n}' reads

$$V(\vec{R}(\vec{n}), \vec{R}'(\vec{n}')) = \frac{1}{|\vec{R}(\vec{n}) - \vec{R}'(\vec{n}')|}. \quad (2.1)$$

The position vector $\vec{R}(\vec{n})$ is given by

$$\vec{R}(\vec{n}) = \vec{X}(\vec{n}) + \vec{r}(\vec{n}). \quad (2.2)$$

Here $\vec{X}(\vec{n})$ is the lattice vector which specifies the centers of the atoms on a rigid fcc lattice, while $\vec{r}(\vec{n})$ is the radius vector of the $4f$ electron; in spherical coordinates $\vec{r}(\vec{n}) = (r(\vec{n}), \Omega(\vec{n}))$, where $\Omega = (\Theta, \phi)$. We perform a multipole expansion of V by using site symmetry adapted functions (SAF's) [25] which transform as irreducible representations of the cubic site point group O_h :

$$V(\vec{R}(\vec{n}), \vec{R}'(\vec{n}')) = \sum_{\Lambda\Lambda'} v_{\Lambda\Lambda'}(\vec{n}, \vec{n}'; r, r') S_{\Lambda}(\vec{n}) S_{\Lambda'}(\vec{n}'), \quad (2.3a)$$

where

$$v_{\Lambda\Lambda'}(\vec{n}, \vec{n}'; r, r') = \int d\Omega(\vec{n}) \int d\Omega(\vec{n}') \frac{S_{\Lambda}(\hat{n}) S_{\Lambda'}(\hat{n}')}{|\vec{R}(\vec{n}) - \vec{R}'(\vec{n}')|}. \quad (2.3b)$$

The SAF's $S_{\Lambda}(\hat{n})$, $\hat{n} \equiv \Omega(\vec{n})$ are linear combinations of spherical harmonics Y_l^m [25]. The index Λ stands for (l, τ) , with $\tau = (\Gamma, \mu, k)$. Here l accounts for the angular dependence of the multipolar expansion, Γ denotes an irreducible representation (in the present case of the group O_h), μ labels the representations that occur more than once and k denotes the rows of a given representation. Expansion (2.3b) still depends on the instantaneous radii $r(\vec{n})$ and $r'(\vec{n}')$. In Ref. I we have written the Coulomb interaction in the space of orientational state vectors $|i\rangle$, $i = 1 - 14$, of the crystal field. The wave functions $\langle \hat{n} | i \rangle$ were taken as linear combinations of spin orbitals $Y_3^m(\Omega) u_s(s_z)$ $m = -3, \dots, +3$, where u_s is the spin

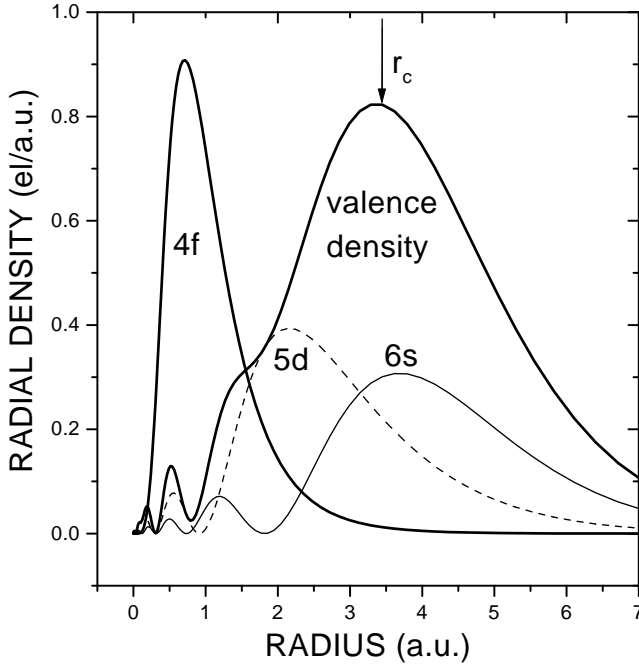


FIG. 1. Calculated radial density distribution for 4f, 5d and 6s electrons of an isolated Ce atom. Valence density is superposition of $(6s)^2$ and 5d; r_c is the close contact radius of γ -Ce.

function, with $s = \pm$ for the spin projections $s_z = \pm 1/2$ on the z -axis respectively. (The consideration of spin orbitals is necessary since we calculate the eigenvalues ε_i of the cubic crystal field in presence of spin-orbit coupling.) Since at present we take into account the radial dependence of the orbitals, we consider basis functions

$$\langle \vec{n}, \vec{r} | i \rangle = \mathcal{R}_f(r(\vec{n})) \langle \hat{n} | i \rangle, \quad (2.4)$$

where we have assumed that the function $\mathcal{R}_f(r)$ is the same for all i . The real radial function $\mathcal{R}_f(r)$ is obtained from a DFT (density functional theory) calculation of an atom of Ce within LDA (local density approximation) for $J = 5/2$ states. In Fig. 1 we plot the radial density for the outer electrons. For a non-relativistic hydrogen-like atom $\mathcal{R}_f(r)$ would correspond to the Laguerre function $\mathcal{R}_{n=4, l=3}(r)$.

The matrix elements of the interaction (2.3a) are obtained as

$$\begin{aligned} & \langle i |_{\vec{n}} \langle i' |_{\vec{n}'} V(\vec{R}(\vec{n}), \vec{R}'(\vec{n}')) | j \rangle_{\vec{n}} | j' \rangle_{\vec{n}'} \\ &= \sum_{\Lambda \Lambda'} v_{\Lambda \Lambda'}^{FF}(\vec{n} - \vec{n}') c_{\Lambda}^F(ij) c_{\Lambda'}^F(i'j'), \end{aligned} \quad (2.5)$$

where

$$\begin{aligned} v_{\Lambda \Lambda'}^{FF}(\vec{n} - \vec{n}') &= \int dr r^2 \int dr' r'^2 \\ &\times \mathcal{R}_f^2(r) \mathcal{R}_f^2(r') v_{\Lambda \Lambda'}(\vec{n}, \vec{n}'; r, r') \end{aligned} \quad (2.6)$$

accounts for the average radial dependence and where

$$c_{\Lambda}^F(ij) = \int d\Omega \langle i | \hat{n} \rangle S_{\Lambda}(\hat{n}) \langle \hat{n} | j \rangle. \quad (2.7)$$

We use the superscript F in order to indicate that we have transitions between two 4f states, *i.e.* $F \equiv (f, f)$. By summing $V(\vec{R}(\vec{n}), \vec{R}'(\vec{n}'))$ over all pairs of lattice sites \vec{n}, \vec{n}' , the total Coulomb interaction operator is then obtained as

$$U^{ff} = \frac{1}{2} \sum'_{\vec{n} \vec{n}'} \sum_{\Lambda \Lambda'} \rho_{\Lambda}^F(\vec{n}) v_{\Lambda \Lambda'}^{FF}(\vec{n} - \vec{n}') \rho_{\Lambda'}^F(\vec{n}'), \quad (2.8)$$

where

$$\rho_{\Lambda}^F(\vec{n}) = \sum_{ij} c_{\Lambda}^F(ij) |i\rangle_{\vec{n}} \langle j|_{\vec{n}}. \quad (2.9)$$

Introducing Fourier transforms

$$\rho_{\Lambda}^F(\vec{q}) = \frac{1}{\sqrt{N}} \sum_{\vec{n}} e^{i\vec{q} \cdot \vec{X}(\vec{n})} \rho_{\Lambda}^F(\vec{n}), \quad (2.10a)$$

$$v_{\Lambda \Lambda'}^{FF}(\vec{q}) = \sum'_{\vec{h} \neq 0} e^{i\vec{q} \cdot \vec{X}(\vec{h})} v_{\Lambda \Lambda'}^{FF}(\vec{h}), \quad (2.10b)$$

where \vec{q} is the wave vector, we get

$$U^{ff} = \frac{1}{2} \sum_{\vec{q}} \sum_{\Lambda \Lambda'} \rho_{\Lambda}^F(\vec{q})^\dagger v_{\Lambda \Lambda'}^{FF}(\vec{q}) \rho_{\Lambda'}^F(\vec{q}). \quad (2.11)$$

The multipolar interaction (2.8) or equivalently (2.11) can be separated into two parts. We recall that $\Lambda \equiv (l, \tau)$.

Firstly we consider the case where $l \neq 0$ and $l' \neq 0$. In I it has been shown that some of the coefficients $c_{\Lambda}^F(ij) \equiv c_l^{\tau}(ij)$ for $l = 2$ and $\tau = (T_{2g}, \mu = 1, k = 1 - 3)$ are different from zero. (We recall that i and j refer to quantum states of the 4f electron). Therefrom we have inferred the existence of quadrupolar ($l = 2$) density fluctuations caused by transitions among 4f electron states. In labeling the quadrupolar T_{2g} functions, we recall that the functions $S_2^k \equiv S_{(l=2, T_{2g}, k)}$ are proportional to the Cartesian components yz, zx and xy for $k = 1, 2$ and 3 respectively. In the basis of real spherical harmonics $Y_l^0, Y_l^{m,c}$ and $Y_l^{m,s}$ of Ref. [25] (see also Eqs. (2.1a)-(2.1c) of I), these functions correspond to $Y_2^{1,s}, Y_2^{1,c}$ and $Y_2^{2,s}$. Writing only the index k for $\Lambda = (l = 2, k)$, we denote the quadrupolar density operator by

$$\rho_k^F(\vec{n}) = \sum_{ij} c_k^F(ij) |i\rangle_{\vec{n}} \langle j|_{\vec{n}}. \quad (2.12)$$

The interaction between quadrupolar 4f electron densities becomes

$$U_{QQ}^{ff} = \frac{1}{2} \sum_{\vec{q}} \sum_{kk'} \rho_k^F(\vec{q})^\dagger v_{kk'}^{FF}(\vec{q}) \rho_{k'}^F(\vec{q}). \quad (2.13)$$

The explicit form of $v_{kk'}^{FF}(\vec{q})$ is discussed in Appendix A.

Secondly we have the case where $l \neq 0$ and $l' = 0$ or vice versa. This means that we consider a multipole l on a given lattice site while the surrounding multipoles on neighboring fcc lattice sites are taken in spherical approximation. This interaction contributes to the crystal field. The crystal field has unit cubic symmetry, the lowest nonzero value of l is 4 and $\tau = (A_{1g}, 1)$, where A_{1g} is the unit representation of the cubic site group O_h . The crystal field contribution from $4f$ electrons at site \vec{n} is then given by

$$V_{CF}^f(\vec{n}) = \frac{12}{\sqrt{4\pi}} \sum_l v_{l,A_{1g}}^F \rho_{l,A_{1g}}^F(\vec{n}). \quad (2.14)$$

Here we have restricted ourselves to the 12 nearest neighbors on the fcc lattice, and $l = 4, 6, \dots$.

The leading contributions to U^{ff} are then given by

$$U^{ff} = U_{QQ}^{ff} + U_{CF}^{ff}, \quad (2.15)$$

where $U_{CF}^{ff} = \sum_{\vec{n}} V_{CF}^f(\vec{n})$. In the following of this section we will discuss the physical consequences of the term U_{QQ}^{ff} , expression (2.13), also called orientational pair quadrupolar interaction. We will give a discussion of the crystal field in Sect. 4.

Previously (I) it has been found that the quadrupole-quadrupole interaction matrix $v^{FF}(\vec{q})$ becomes diagonal and has a twofold degenerate negative eigenvalue called $\lambda_{X_5^+}$ at the X point of Brillouin zone (BZ) of the fcc lattice (see also Appendix A). This attractive interaction induces an orientational ordering of the quadrupolar densities in a $Pa\bar{3}$ structure. A condensation scheme for the phase transition $Fm\bar{3}m \rightarrow Pa\bar{3}$ reads:

$$\bar{\rho}_3^F(\vec{q}_x^X) = \bar{\rho}_1^F(\vec{q}_y^X) = \bar{\rho}_2^F(\vec{q}_z^X) = \bar{\rho}^F \sqrt{N} \neq 0, \quad (2.16a)$$

$$\bar{\rho}_2^F(\vec{q}_x^X) = \bar{\rho}_3^F(\vec{q}_y^X) = \bar{\rho}_1^F(\vec{q}_z^X) = 0. \quad (2.16b)$$

Here the bar stands for a thermal expectation value, while $\bar{\rho}^F$ is the order parameter amplitude. The above condensation scheme corresponds to one of eight possible domains of $Pa\bar{3}$. The wave vectors \vec{q}_x^X , \vec{q}_y^X and \vec{q}_z^X stand for $(2\pi/a)(1, 0, 0)$, $(2\pi/a)(0, 1, 0)$ and $(2\pi/a)(0, 0, 1)$ respectively, where a is the cubic lattice constant. For each arm of the star of $^*\vec{q}^X = \{\vec{q}_x^X, \vec{q}_y^X, \vec{q}_z^X\}$ there are two basis functions $\bar{\rho}_k^F$. Hence the functions $\rho_k^F(\vec{q}^X)$ of the condensation scheme (2.16a,b) form a basis of the six dimensional irreducible representation X_5^+ of the space group $Fm\bar{3}m$. In real space the ordering implies four sublattices of simple cubic structure as shown in figure 3 of Ref. I.

In I, where we have taken a fixed radius r_f for the $4f$ radial distribution, we found the eigenvalue $\lambda_{X_5^+} = -3491$ K (Kelvin) and a phase transition temperature $T_1 = 85.6$ K. At present we have calculated the eigenvalue $\lambda_{X_5^+} = -4\gamma^{FF}$ (see Appendix A) with the radial dependence $\mathcal{R}_f(r)$ in Eq. (2.6) taken from an atomic

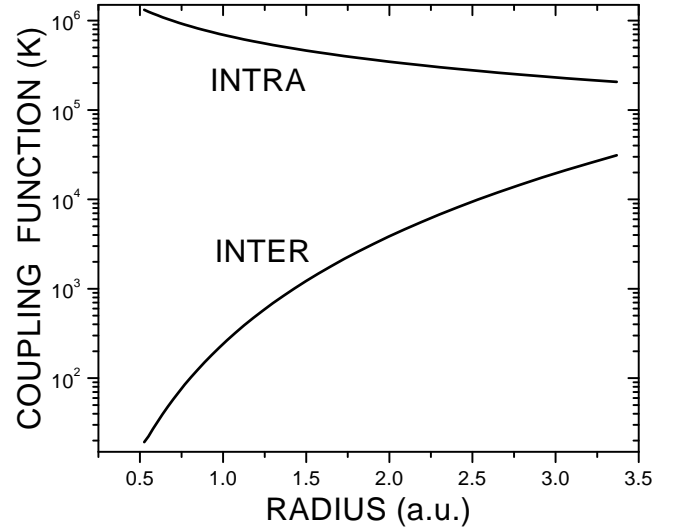


FIG. 2. Radial dependence of quadrupole-quadrupole interactions

$v_{\Lambda\Lambda'}(\vec{n}, \vec{n}'; r, r')$, where $r = r'$, and $\Lambda = \Lambda' = (l = 2, T_{2g}, k)$; $\vec{n} = \vec{n}'$ (intra-, $k = 1, 2, 3$) and $\vec{n} \neq \vec{n}'$ (inter- on fcc lattice) with $\vec{n} = (0, 0, 0)$, $\vec{n}' = (a/2)(0, 1, 1)$, $k = 1$.

DFT calculation with LDA. Although the atomic $4f$ electron density is small beyond the close contact radius $r_c = a/(2\sqrt{2}) = 3.448$ a.u., the opposite holds for the inter-site interaction potential $v_{\Lambda\Lambda'}(\vec{n}, \vec{n}'; r, r')$ and its first derivative (see below), which increase substantially when $r \rightarrow r_c$ and $r' \rightarrow r_c$ (see Fig. 2). We have investigated several models for the radial integral (2.6). In model 1 we consider the radial integration in the range $0 < r < r_c$, that is without any overlap of the atomic $4f$ electronic densities of neighboring atoms, and we obtain $\lambda_{X_5^+} = -2121$ K, next (model 2) we have allowed for an overlap between neighboring sites and extended the integration over the range $0 \leq r \leq \infty$. We then obtain $\lambda_{X_5^+} = -2478$ K. Finally (model 3) we assume again the integration range $0 \leq r \leq r_c$ but renormalize the $4f$ electronic density to unity. The result for $\lambda_{X_5^+}$ is -2682 K. Comparing these values with $\lambda_{X_5^+} = -3491$ K obtained for the calculation with the characteristic radius r_f , we conclude that a refinement of the theory in smearing out the radial extension of the $4f$ electron distribution does not increase the strength of the quadrupole-quadrupole interaction and consequently does not increase the transition temperature.

So far we have considered multipolar interactions on a rigid lattice. In order to account for the lattice contraction at the $\gamma - \alpha$ phase transition, we have to include lattice displacements. In I we have shown that the inter-site quadrupolar interaction is modified by lattice displacements $u_\nu(\vec{n})$. The correction to the potential reads

$$U_{QQT} = \frac{1}{2} \sum_{\vec{n}\vec{n}'}' \sum_{\nu} \sum_{kk'} v'_{\nu kk'}(\vec{n} - \vec{n}'; r, r')$$

$$\times S_2^k(\hat{n}) S_2^{k'}(\hat{n}') [u_\nu(\vec{n}) - u_\nu(\vec{n}')]. \quad (2.17)$$

Here S_2^k are SAF's with $l = 2$, T_{2g} , $k = 1 - 3$. The coupling coefficients $v'_{\nu kk'}$ are given by the derivative of the quadrupole-quadrupole interaction with respect to lattice displacements:

$$v'_{\nu kk'}(\vec{n} - \vec{n}'; r, r') = \int d\Omega(\vec{n}) \int d\Omega(\vec{n}') S_2^k(\hat{n}) S_2^{k'}(\hat{n}') \times \frac{\partial}{\partial X_\nu(\vec{n})} \frac{1}{|\vec{R}(\vec{n}) - \vec{R}'(\vec{n}')|}. \quad (2.18)$$

Previously (I) this expression was considered for $4f$ electrons on a shell with the (fixed) characteristic radius $r = r' = r_f$. Defining

$$V'_\nu(\vec{R}(\vec{n}), \vec{R}'(\vec{n}')) = \sum_{kk'} v'_{\nu kk'}(\vec{n} - \vec{n}'; r, r') S_2^k(\hat{n}) S_2^{k'}(\hat{n}') \quad (2.19)$$

we now consider matrix elements with basis functions (2.4) and obtain

$$\langle i|\vec{n}\langle i'|\vec{n}'|V'_\nu(\vec{R}(\vec{n}), \vec{R}'(\vec{n}'))|j\rangle_{\vec{n}}|j'\rangle_{\vec{n}'} = \sum_{kk'} v'_{\nu kk'}(\vec{n} - \vec{n}') c_k^F(ij) c_{k'}^F(i'j'), \quad (2.20)$$

where

$$v'_{\nu kk'}(\vec{n} - \vec{n}') = \int dr r^2 \int dr' r'^2 \mathcal{R}_f^2(r) \mathcal{R}_f^2(r') \times v'_{\nu kk'}(\vec{n} - \vec{n}'; r, r'). \quad (2.21)$$

The correction to the quadrupolar interaction between $4f$ electrons then becomes

$$U_{QQT}^{ff} = \frac{1}{2} \sum'_{\vec{n}\vec{n}'} \rho_k^F(\vec{n}) v'_{\nu kk'}(\vec{n} - \vec{n}') \rho_{k'}^F(\vec{n}') \times [u_\nu(\vec{n}) - u_\nu(\vec{n}')], \quad (2.22)$$

with summation over repeated indices k, k', ν . We introduce the Fourier expansion

$$u_\nu(\vec{n}) = (Nm)^{-1/2} \sum_{\vec{q}} u_\nu(\vec{q}) e^{i\vec{q} \cdot \vec{X}(\vec{n})}, \quad (2.23)$$

where m is the Ce mass. Using definition (2.10a), we rewrite expression (2.22) in Fourier space. In the long wavelength limit $\vec{q} \rightarrow 0$ and taking \vec{p} close to the star of \vec{p}^X , we obtain

$$U_{QQT}^{ff} = i \sum_{\vec{p}\vec{q}} \sum'_{\nu(k)} v'_{\nu kk'}(\vec{q}, \vec{p}) \rho_k^F(\vec{p})^\dagger \rho_{k'}^F(\vec{p}) u_\nu(\vec{q}). \quad (2.24)$$

Here the sum \sum' refers to $\nu = x, y$ for $k=3$, to $\nu = z, x$ for $k=2$ and to $\nu = z, y$ for $k=1$. The coupling matrix is obtained as

$$v'_{\nu 33}{}^{FF}(\vec{q}, \vec{p}) = (Nm)^{-1/2} \Lambda^{FF} q_\nu a \cos\left(\frac{p_x a}{2}\right) \cos\left(\frac{p_y a}{2}\right), \quad (2.25)$$

with $\Lambda^{FF} = v'_{\nu 33}{}^{FF}(\vec{n} - \vec{n}')$, where $\nu = x$ or y and $\vec{X}(\vec{n}) - \vec{X}(\vec{n}') = (a/2)(1, 1, 0)$ on the fcc lattice (for more details, see Ref. I). The other elements of $v'_{\nu kk'}{}^{FF}(\vec{q}, \vec{p})$ follow by symmetry considerations and permutation of indices.

We consider expression (2.24) in the $Pa\bar{3}$ ordered phase by using the condensation scheme (2.16a). The lattice displacements are taken in the long wavelength limit where they are related to the homogeneous strains. Symmetry implies that only longitudinal strains occur:

$$\lim_{\vec{q} \rightarrow 0} i q_\nu \bar{u}_\nu(\vec{q}) = \sqrt{mN} \epsilon_{\nu\nu}, \quad \nu = x, y, z. \quad (2.26)$$

Then U_{QQT} becomes

$$\frac{1}{N} U_{QQT}^{ff} = -2a \Lambda^{FF} (\bar{\rho}^F)^2 \sum_{\nu} \epsilon_{\nu\nu}, \quad (2.27)$$

which corresponds to a coupling of ordered quadrupoles (quadratic) to longitudinal strains. Notice that the sign of Λ^{FF} is negative, this is a consequence of the repulsive nature of quadrupole-quadrupole interaction. The strains give rise to an elastic energy of the cubic lattice:

$$\frac{1}{N} U_{TT} = \frac{a^3}{4} [c_{11}^0 (\epsilon_{xx}^2 + \epsilon_{yy}^2 + \epsilon_{zz}^2) + 2c_{12}^0 (\epsilon_{xx}\epsilon_{yy} + \epsilon_{yy}\epsilon_{zz} + \epsilon_{zz}\epsilon_{xx})]. \quad (2.28)$$

Here c_{11}^0 and c_{12}^0 are the bare elastic constants. The interplay of quadrupolar order and lattice displacements follows from the interaction Hamiltonian

$$U = U_{TT} + U_{QQ}^{ff} + U_{QQT}^{ff}. \quad (2.29)$$

Minimizing $U[\bar{\rho}^F, \epsilon_{\nu\nu}]$ with respect to the strains for a given $Pa\bar{3}$ ordered structure, we obtain $\epsilon_{\nu\nu}$,

$$\epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz} = -8a^{-2} |\Lambda^{FF}| \kappa_L (\bar{\rho}^F)^2, \quad (2.30)$$

while the change of the lattice constant is given by $\Delta a = \epsilon_{xx} a$. Here $\kappa_L = (c_{11}^0 + 2c_{12}^0)^{-1}$ is the linear compressibility. Hence the present theory leads unambiguously to a lattice contraction. In order to provide a numerical estimate of the lattice contraction, one has to calculate Λ^{FF} , to estimate κ_L from experimental results and to calculate by the methods of statistical mechanics the discontinuity of the order parameter at the $\gamma - \alpha$ phase transition. In I (fixed radius r_f) we did obtain $\Lambda^{FF} = -445$ K/a.u. (-841 K/Å) [22]. Now, for the models 1), 2), and 3) of the spatial radial integrals we obtain $\Lambda^{FF} = -498, -581$ and -659 K/Å respectively. We conclude that the present refinement in calculating Λ^{FF} is not helpful in view of obtaining a larger value of Λ^{FF} and hence of the lattice contraction Δa . Since our theoretical value of Δa is more than one order of magnitude

too small to account for the $\sim 15\%$ volume contraction of cerium, we conclude that a significant process has so far been omitted in our treatment. In the following section we will study the effect of conduction electrons on quadrupolar interactions.

III. MULTIPOLAR INTERACTIONS

Here we will investigate about the existence of multipolar interactions between the localized $4f$ electrons and the $(6s5d)^3$ conduction electrons U^{fc} as well as multipolar interactions among conduction electrons U^{cc} .

As a consequence of Bloch's theorem the conduction electron states are classified according to the irreducible representations of the translational symmetry group of the crystal. Nevertheless, in the proximity of the nuclei the corresponding wave functions can be expanded in terms of spherical harmonics. This fact reflects the importance of Coulomb singularities associated with the nuclei. In the following we will focus on the interactions inside the "muffin-tin" or touching spheres centered on the nuclei and for the description of itinerant states adopt the tight-binding approximation. In absence of a static magnetic field, conduction electronic states with spin projections $s_z = \pm 1/2$ are degenerate. Hence we will omit the spin dependence of the wave function. The wave function of a conduction electron with wave vector \vec{k} and band index α is then written as a linear combination of local atomic wave functions

$$\langle \vec{R} | \vec{k}, \alpha \rangle = \psi_{\vec{k}, \alpha}(\vec{R}) = \frac{1}{\sqrt{N}} \sum_{\vec{n}'} e^{i\vec{k}\vec{X}(\vec{n}')} \sum_{lm} \gamma_{lm}(\vec{k}, \alpha) \phi_{lm}(\vec{R} - \vec{X}(\vec{n}')), \quad (3.1)$$

where the position vector \vec{R} is given by Eq. (2.2). The atomic wave functions are given by $\phi_{lm}(\vec{r}) = \mathcal{R}_l(r) Y_l^m(\Omega)$. The expansion coefficients $\gamma_{lm}(\vec{k}, \alpha)$ and corresponding eigenvalues $E(\vec{k}, \alpha)$ are obtained by solving the secular equation (see e.g. [48])

$$\sum_{\lambda} \left(H_{\lambda\lambda'}(\vec{k}) - E(\vec{k}, \alpha) S_{\lambda\lambda'}(\vec{k}) \right) \gamma_{\lambda'}(\vec{k}, \alpha) = 0. \quad (3.2)$$

Here $H(\vec{k})$ and $S(\vec{k})$ are matrices of single particle Hamiltonian and overlap, respectively. Here and in the following $\lambda = (l, m)$, $\delta_{\lambda\lambda'} = \delta_{ll'} \delta_{mm'}$. The eigenvalues $E(\vec{k}, \alpha)$ refer to the energy band spectrum of the conduction electrons. Notice that the wave function $\psi_{\vec{k}, \alpha}(\vec{R})$ satisfies the Bloch condition. In the following we shall use an idealized basis set of orthogonal Wannier functions $\phi_{\lambda}(\vec{r}(\vec{n})) = \langle \vec{R} | \lambda \rangle_{\vec{n}}$ without overlap,

$$\vec{n} \langle \lambda | \lambda' \rangle_{\vec{n}'} = \delta_{\lambda\lambda'} \delta_{\vec{n}\vec{n}'}. \quad (3.3)$$

The coefficients γ_{λ} satisfy the relation

$$\sum_{\lambda} \gamma_{\lambda}^*(\vec{k}, \alpha) \gamma_{\lambda}(\vec{k}', \alpha') = \delta_{\vec{k}\vec{k}'} \delta_{\alpha\alpha'}. \quad (3.4)$$

The functions $\psi_{\vec{k}, \alpha}(\vec{R})$ are then normalized:

$$\langle \vec{k}, \alpha | \vec{k}', \alpha' \rangle = \delta_{\vec{k}\vec{k}'} \delta_{\alpha\alpha'}. \quad (3.5)$$

The corresponding electronic Hamiltonian in second quantization is

$$U_0^c = \sum_{\vec{k}\alpha} E_{\vec{k}\alpha} a_{\vec{k}\alpha}^{\dagger} a_{\vec{k}\alpha}, \quad (3.6)$$

where $a_{\vec{k}\alpha}^{\dagger}$ and $a_{\vec{k}\alpha}$ are creation and annihilation operators for one electron in state (\vec{k}, α) .

In case of cerium, we will restrict ourselves to conduction electrons of d type ($l = 2$, $m = -2, \dots, +2$, with principal quantum number $n=5$) and of s type ($l=0$, $m=0$, with $n=6$). Fig. 1 shows the radial density of the valence electrons of a Ce atom, it should also be a guide of the relative spatial extension of the localized $4f$ and the conduction electrons in the crystal.

Although the derivation of multipolar interactions presented later in this Section is general in the following we imply the high temperature γ phase of cerium. There the total electronic density associated with the conduction electrons has the symmetry of the space group $Fm\bar{3}m$ [21]. At each lattice site the band electronic density has on average the unit symmetry (A_{1g}) of the cubic point group O_h . It is important to realize that the on-site quadrupolar charge density fluctuations of T_{2g} and E_g symmetry do not interact with the totally symmetric charge distribution (A_{1g}) representing the ground state of cerium (see also Eq. (3.11)). On one hand this allows us to use the Landau concept of Fermi liquid and to consider the conduction electrons described by Eq. (3.1) as quasiparticles where the ground state on-site interactions have already been taken into account through the coefficients $\gamma_{lm}(\vec{k}, \alpha)$. On the other hand we can focus only on the quadrupolar interactions where conduction electrons are involved and consider these interactions separately from the ground state.

Interactions involving conduction electrons will be described within the formalism of second quantization. We introduce field operators

$$\Psi(\vec{R}) = \sum_{\vec{k}\alpha} a_{\vec{k}\alpha} \langle \vec{R} | \vec{k}\alpha \rangle, \quad (3.7a)$$

$$\Psi^{\dagger}(\vec{R}) = \sum_{\vec{k}\alpha} a_{\vec{k}\alpha}^{\dagger} \langle \vec{k}\alpha | \vec{R} \rangle. \quad (3.7b)$$

The operators Ψ and Ψ^{\dagger} satisfy the usual anticommutation relations for fermion fields. Although the derivation of multipolar expansions for these interactions is analogous, in particular as far as symmetry is concerned, to the procedure of Sect. 2, there is an essential difference. Since

the conduction electrons are not localized, they give rise to quadrupolar pair interactions on a same site (intra) and to interactions between different sites (inter).

The Coulomb interaction between localized $4f$ electrons at sites $\{\vec{n}\}$ and the conduction electrons is given by

$$U^{fc} = \sum_{\vec{n}} \sum_{ij} |i\rangle_{\vec{n}} \langle j|_{\vec{n}} \times \int d\vec{R}' \Psi^\dagger(\vec{R}') \langle i|_{\vec{n}} V(\vec{R}(\vec{n}), \vec{R}') |j\rangle_{\vec{n}} \Psi(\vec{R}'). \quad (3.8)$$

We observe that $\int d\vec{R}' \rightarrow \sum_{\vec{n}'} \int d\vec{r}'$, where the integral extends over the volume of the cell \vec{n}' . In expression (3.8) we perform a multipole expansion of V similar to Eqs. (2.3a,b) and then calculate matrix elements

$$\begin{aligned} \langle i|_{\vec{n}} \langle \vec{k}, \alpha | V(\vec{R}(\vec{n}), \vec{R}'(\vec{n}')) | j\rangle_{\vec{n}} | \vec{p}, \beta \rangle &= \frac{e^{i(\vec{p}-\vec{k}) \cdot \vec{X}(\vec{n}')}}{N} \\ &\times \sum_{\Lambda \Lambda'} \sum_{l_1 l_2} v_{\Lambda \Lambda'}^{F l_1 l_2}(\vec{n} - \vec{n}') c_{\Lambda}^F(ij) c_{\Lambda' l_1 l_2}(\vec{k}, \alpha; \vec{p}, \beta). \end{aligned} \quad (3.9)$$

Here we define

$$\begin{aligned} v_{\Lambda \Lambda'}^{F l_1 l_2}(\vec{n} - \vec{n}') &= \int dr r^2 \int dr' r'^2 \mathcal{R}_f^2(r) \\ &\times v_{\Lambda \Lambda'}(\vec{n}, \vec{n}'; r, r') \mathcal{R}_{l_1}(r') \mathcal{R}_{l_2}(r'), \end{aligned} \quad (3.10a)$$

$$\begin{aligned} c_{\Lambda' l_1 l_2}(\vec{k}, \alpha; \vec{p}, \beta) &= \sum_{m_1 m_2} \gamma_{l_1 m_1}^*(\vec{k}, \alpha) \gamma_{l_2 m_2}(\vec{p}, \beta) \\ &\times c_{\Lambda'}(l_1 m_1, l_2 m_2), \end{aligned} \quad (3.10b)$$

and

$$c_{\Lambda'}(l_1 m_1, l_2 m_2) = \int Y_{l_1}^{m_1 *}(\Omega) S_{\Lambda'}(\Omega) Y_{l_2}^{m_2}(\Omega) d\Omega. \quad (3.10c)$$

In the following we will introduce a single index L for (l_1, l_2) , writing $v_{\Lambda \Lambda'}^{F L}$ for $v_{\Lambda \Lambda'}^{F l_1 l_2}$, $c_{\Lambda' L}$ for $c_{\Lambda' l_1 l_2}$ etc.. We notice that the index $l_1(l_2)$ takes the values 0 and 2 corresponding to s and d electrons. We recall that $c_{\Lambda}^F(ij)$, referring to the $4f$ electron transitions, is given by expression (2.7).

Since the conduction electrons are delocalized, we will have to distinguish between interactions where $\vec{n} \neq \vec{n}'$ (inter-site), and where $\vec{n} = \vec{n}'$ (on-site). In the first case $v_{\Lambda \Lambda'}(\vec{n}, \vec{n}'; r, r')$ is given by an expression of type (2.3b), in the second case we have

$$\begin{aligned} v_{\Lambda \Lambda'}(\vec{n} = \vec{n}'; r, r') &= \int d\Omega \int d\Omega' \frac{1}{|\vec{r} - \vec{r}'|} S_{\Lambda}(\Omega) S_{\Lambda'}(\Omega') \\ &= \left(\frac{r_{<}^l}{r_{>}^{l+1}} \right) \frac{4\pi}{2l+1} \delta_{\Lambda \Lambda'}, \end{aligned} \quad (3.11)$$

which is independent of the site, as is also the case for $v_{\Lambda \Lambda'}^{F L}(\vec{n} = \vec{n}')$. Here $r_{>} = \max(r, r')$, $r_{<} = \min(r, r')$ and $\delta_{\Lambda \Lambda'} = \delta_{\tau \tau'} \delta_{ll'}$. The inter-site coupling $v_{\Lambda \Lambda'}^{F L}(\vec{n} - \vec{n}')$ still depends on the distance $|\vec{X}(\vec{n}) - \vec{X}(\vec{n}')|$, as follows from the translational invariance of the lattice.

In addition to the multipole density of $4f$ electrons $\rho_{\Lambda}^F(\vec{q})$, Eq. (2.10a), we define the multipole density of conduction electrons

$$\rho_{\Lambda}^L(\vec{n}) = \frac{1}{\sqrt{N}} \sum_{\vec{q}} \rho_{\Lambda}^L(\vec{q}) e^{-i\vec{q} \cdot \vec{X}(\vec{n})}, \quad (3.12a)$$

$$\rho_{\Lambda}^L(\vec{q}) = \frac{1}{\sqrt{N}} \sum_{\alpha \beta} \sum_{\vec{k}} a_{\vec{k} \alpha}^\dagger a_{\vec{k} - \vec{q} \beta} c_{\Lambda L}(\vec{k}, \alpha; \vec{k} - \vec{q}, \beta). \quad (3.12b)$$

The interaction for the inter-site contribution of U^{fc} is then given by

$$U^{fc}|_{inter} = \sum_{\vec{q}} \rho_{\Lambda}^F(\vec{q})^\dagger v_{\Lambda \Lambda'}^{F L}(\vec{q}) \rho_{\Lambda'}^L(\vec{q}), \quad (3.13a)$$

with

$$v_{\Lambda \Lambda'}^{F L}(\vec{q}) = \sum_{\vec{h} \neq 0} e^{i\vec{q} \cdot \vec{X}(\vec{h})} v_{\Lambda \Lambda'}^{F L}(\vec{h}). \quad (3.13b)$$

The on-site part of U^{fc} is obtained as

$$U^{fc}|_{intra} = C_{\Lambda \Lambda'}^F \sum_{\vec{q}} \rho_{\Lambda}^F(\vec{q})^\dagger \rho_{\Lambda'}^L(\vec{q}), \quad (3.14a)$$

where

$$C_{\Lambda \Lambda'}^F = v_{\Lambda \Lambda'}^{F L}(\vec{n} = \vec{n}'). \quad (3.14b)$$

Here we have also used the orthogonality relation (3.11). In expressions (3.13a) and (3.14a), summation is understood over indices $\Lambda, \Lambda', L(l_1, l_2)$.

In a similar way we treat the multipolar interactions between conduction electrons. We now start from the expression in operator representation

$$U^{cc} = \frac{1}{2} \int d\vec{R}' \int d\vec{R} \Psi^\dagger(\vec{R}') \Psi^\dagger(\vec{R}) V(\vec{R}, \vec{R}') \Psi(\vec{R}) \Psi(\vec{R}'). \quad (3.15)$$

We have to consider matrix elements

$$\begin{aligned} \langle \vec{k}, \alpha | \langle \vec{k}', \alpha' | V(\vec{R}, \vec{R}') | \vec{p}, \beta \rangle | \vec{p}', \beta' \rangle &= \\ \sum_{\vec{n} \vec{n}'} \sum_{\Lambda \Lambda'} \sum_L \sum_{L'} v_{\Lambda \Lambda'}^{L' L}(\vec{n} - \vec{n}') c_{\Lambda L}(\vec{k}, \alpha; \vec{p}, \beta) \\ &\times c_{\Lambda' L'}(\vec{k}', \alpha'; \vec{p}', \beta') \frac{e^{i(\vec{p}-\vec{k}) \cdot \vec{X}(\vec{n})}}{N} \frac{e^{i(\vec{p}'-\vec{k}') \cdot \vec{X}(\vec{n}')}}{N}, \end{aligned} \quad (3.16)$$

where

$$\begin{aligned} v_{\Lambda \Lambda'}^{L' L}(\vec{n} - \vec{n}') &= \int dr r^2 \int dr' r'^2 \mathcal{R}_{l_1}(r) \mathcal{R}_{l_2}(r) \\ &\times v_{\Lambda \Lambda'}(\vec{n}, \vec{n}'; r, r') \mathcal{R}_{l_1'}(r') \mathcal{R}_{l_2'}(r'). \end{aligned} \quad (3.17)$$

Again we distinguish inter- site and intra- site interactions. We obtain for the inter- site contribution

$$U^{cc}|_{inter} = \frac{1}{2N} \sum_{\vec{k}\vec{k}'\vec{q}} a_{\vec{k}\alpha}^\dagger a_{\vec{k}'\alpha'}^\dagger a_{\vec{k}'-\vec{q}\beta} a_{\vec{k}+\vec{q}\beta'} \times v_{\Lambda\Lambda'}^{L\ L'}(\vec{q}) c_{\Lambda L}(\vec{k}, \alpha; \vec{k} + \vec{q}, \beta) \times c_{\Lambda' L'}(\vec{k}', \alpha'; \vec{k}' - \vec{q}, \beta'), \quad (3.18a)$$

with

$$v_{\Lambda\Lambda'}^{L\ L'}(\vec{q}) = \sum_{\vec{h} \neq 0} e^{i\vec{q} \cdot \vec{X}(\vec{h})} v_{\Lambda\Lambda'}^{L\ L'}(\vec{h}). \quad (3.18b)$$

In Eq. (3.18a) summation is understood over the indices $\alpha, \dots, L(l_1, l_2), \dots, \Lambda, \dots$. Expression (3.18a) can be rewritten as

$$U^{cc}|_{inter} = \frac{1}{2} \sum_{\vec{q}} v_{\Lambda\Lambda'}^{L\ L'}(\vec{q}) \eta \left(\rho_{\Lambda}^L(\vec{q})^\dagger \rho_{\Lambda'}^{L'}(\vec{q}) \right), \quad (3.19)$$

where $\rho_{\Lambda}^L(\vec{q})$ is given by Eq. (3.12b) and where η is the normally ordered product operator such that all the a^\dagger are placed to the left and all a to the right in the product.

The on-site contribution is given by

$$U^{cc}|_{intra} = \frac{1}{2} C_{\Lambda\Lambda}^{L\ L'} \sum_{\vec{q}} \eta \left(\rho_{\Lambda}^L(\vec{q})^\dagger \rho_{\Lambda}^{L'}(\vec{q}) \right), \quad (3.20a)$$

with

$$C_{\Lambda\Lambda}^{L\ L'} = v_{\Lambda\Lambda}^{L\ L'}(\vec{n} = \vec{n}'). \quad (3.20b)$$

So far the present formalism is general as far as multipoles are concerned. In the following of this section we will study the interaction between quadrupoles ($l = 2, l' = 2$). In Sect. 4 we will study the crystal field ($l = 4, l' = 0$).

We consider the three quadrupolar components of T_{2g} symmetry and write the index k for $\Lambda = (l = 2, k)$, with $k = 1 - 3$. The quadrupolar density of conduction electrons becomes

$$\rho_k^L(\vec{q}) = \frac{1}{\sqrt{N}} \sum_{\alpha\beta} \sum_{\vec{p}} a_{\vec{p}\alpha}^\dagger a_{\vec{p}-\vec{q}\beta} c_{kL}(\vec{p}, \alpha; \vec{p} - \vec{q}, \beta). \quad (3.21)$$

We observe that $c_{kL}(\vec{p}, \alpha; \vec{p} - \vec{q}, \beta)$ comprises the factor $c_k(l_1 m_1, l_2 m_2)$ which is defined (compare with expressions (3.10b) and (3.10c)) by

$$c_k(l_1 m_1, l_2 m_2) = \int Y_{l_1}^{m_1*}(\Omega) S_2^k(\Omega) Y_{l_2}^{m_2}(\Omega) d\Omega. \quad (3.22)$$

The quadrupolar contributions from the interaction potentials (3.13a), (3.14a) between $4f$ electrons and conduction electrons then read

TABLE I. Calculated coefficients $c_k(l_1 m_1, l_2 m_2)$, $k = 1 - 3$, $l_1 = l_2 = 2$; m_i ($i = 1, 2$) stands for the indices (m_i, c) or (m_i, s) of real spherical harmonics [25] Those functions which are not quoted here give zero contributions.

| (m) | (m') | $\tau = (T_{2g}, 1)$ | $(T_{2g}, 2)$ | $(T_{2g}, 3)$ |
|-------|--------|----------------------|---------------|---------------|
| (0,c) | (1,c) | 0 | 0.09011 | 0 |
| (0,c) | (1,s) | 0.09011 | 0 | 0 |
| (0,c) | (2,s) | 0 | 0 | -0.18022 |
| (1,c) | (1,s) | 0 | 0 | 0.15608 |
| (1,c) | (2,c) | 0 | 0.15608 | 0 |
| (1,c) | (2,s) | 0.15608 | 0 | 0 |
| (1,s) | (2,c) | -0.15608 | 0 | 0 |
| (1,s) | (2,s) | 0 | 0.15608 | 0 |

$$U_{QQ}^{fc}|_{inter} = \sum_{\vec{q}} \rho_k^F(\vec{q})^\dagger v_k^{F\ L'}(\vec{q}) \rho_{k'}^L(\vec{q}), \quad (3.23a)$$

and

$$U_{QQ}^{fc}|_{intra} = C_{k\ k}^{F\ L} \sum_{\vec{q}} \rho_k^F(\vec{q})^\dagger \rho_k^L(\vec{q}). \quad (3.23b)$$

The contribution of the quadrupolar pair interaction potential to expression (3.8) is then given by

$$U_{QQ}^{fc} = U_{QQ}^{fc}|_{inter} + U_{QQ}^{fc}|_{intra} \quad (3.24)$$

The quadrupolar interactions between conduction electrons follow from Eqs. (3.19) and (3.20a):

$$U_{QQ}^{cc}|_{inter} = \frac{1}{2} \sum_{\vec{q}} v_k^{L\ L'}(\vec{q}) \eta \left(\rho_k^L(\vec{q})^\dagger \rho_{k'}^{L'}(\vec{q}) \right), \quad (3.25a)$$

$$U_{QQ}^{cc}|_{intra} = \frac{1}{2} C_{k\ k}^{L\ L'} \sum_{\vec{q}} \eta \left(\rho_k^L(\vec{q})^\dagger \rho_k^{L'}(\vec{q}) \right). \quad (3.25b)$$

The contribution to expression (3.15) is given by

$$U_{QQ}^{cc} = U_{QQ}^{cc}|_{inter} + U_{QQ}^{cc}|_{intra} \quad (3.26)$$

In order to select the contribution from conduction electrons, we have studied the coefficients $c_k(l_1 m_1, l_2 m_2)$. We find it convenient to use as basis functions for the conduction electron states the real spherical harmonics (see Sect. II). Then the s electron state is $|l = 0, m = 0\rangle$ while the five d electron states are $|2, m = 0\rangle$; $|2, (m, s)\rangle$, $|2, (m, c)\rangle$, $m = 1, 2$. There are no transitions between $6s$ states, the transitions between $6s$ and $5d$ states are

$$\begin{aligned} \langle 0, 0 | S_2^1 | 2, (1, s) \rangle &= \langle 0, 0 | S_2^2 | 2, (1, c) \rangle \\ &= \langle 0, 0 | S_2^3 | 2, (2, s) \rangle = \frac{1}{\sqrt{4\pi}} \end{aligned} \quad (3.27)$$

and zero otherwise. The transition elements between $5d$ states are quoted in Table 1.

TABLE II. Interaction parameters C^{AB} , λ^{AB} and Λ^{AB} calculated with s -, d -, f - atomic radial distributions and lattice constant $a=9.753$ a.u.(γ -Ce); $A = (l_1 l_2)$, $B = (l'_1 l'_2)$, $F = (ff)$.

| $l_1 l_2$ | $l'_1 l'_2$ | C (in K) | λ (in K) | Λ (in K/ \bar{A}) |
|-----------|-------------|-------------|------------------|------------------------------|
| ff | ff | - | -2121 | -498 |
| sd | ff | ± 4408 | -3924 | -950 |
| dd | ff | 75389 | -6025 | -1459 |
| dd | dd | 94559 | -17695 | -4283 |
| ds | ds | 21297 | -7547 | -1822 |
| ds | dd | ± 34858 | -11545 | -2792 |

Since the coefficients $c_k(l_1 m_1, l_2 m_2)$ always occur in conjunction with interaction matrix elements $v_k^{l_1 l_2 l'_1 l'_2}$ ($v_k^{L L'}$), we can immediately select the relevant matrix elements. We observe that the indices l_1 and l_2 in the interaction matrix elements then directly refer to s or d electrons and we will adopt the notation $v_k^{sd dd}$, $v_k^{ff sd}$ etc.. The indices f , s and d of these interaction matrix elements refer only to the radial dependence, they are irrelevant for symmetry considerations. The structure of the intersite quadrupole-quadrupole interaction matrices are investigated in Appendix A. From Eq. (3.11) it follows that the on-site elements $C_k^{F L}$ are diagonal in k , k' and equal for $k=1,2,3$; the same holds for $C_k^{L L'}$. In the following we omit the indices k , k' and write $C^{ff sd}$, $C^{sd sd}$ etc.. Numerical values are given in Table 2. By introducing quadrupolar pair interactions on a same site we generalize the concept of spherically symmetric on-site electron-electron repulsions which is a characteristic property of strongly correlated electron systems.

In order to treat the effect of conduction electrons on the lattice contraction, we have studied the coupling of quadrupole-quadrupole interactions with lattice displacements within the tight-binding approach. We start from expression U_{QQT} , Eq. (2.17), and remind that $u_\nu(\vec{n})$ and $u_\nu(\vec{n}')$ refer to lattice displacements at different sites. We first consider matrix elements of V'_ν , expression (2.19), between $4f$ electron and conduction electron states. We proceed in analogy with Eqs. (3.8)-(3.13b) but retain only inter-site contributions. We then find (compare with Eq. (5.13) of I) in the long wavelength limit $\vec{q} \rightarrow 0$, and \vec{p} close to the star of \vec{p}^X :

$$U_{QQT}^{fc} = 2i \sum_{\vec{p}\vec{q}} \sum'_{\nu(k)} v_{\nu k}^{F L}(\vec{q}, \vec{p}) \rho_k^F(-\vec{p}) \rho_k^L(\vec{p}) u_\nu(\vec{q}). \quad (3.28)$$

Here the sum \sum' refers to $\nu = x, y$ for $k=3$; to $\nu = z, x$ for $k = 2$ and to $\nu = z, y$ for $k = 1$. The coupling matrix is obtained as

$$v_{\nu 3}^{F L}(\vec{q}, \vec{p}) = \frac{1}{\sqrt{Nm}} \Lambda^{F L} q_\nu a \cos\left(\frac{p_x a}{2}\right) \cos\left(\frac{p_y a}{2}\right), \quad (3.29)$$

with $\Lambda^{F L}$ given by $v_{\nu k}^{F L}(\vec{n} - \vec{n}')$, where $\nu = x$ or y , $k = 3$ and $\vec{X}(\vec{n}) - \vec{X}(\vec{n}') = (a/2)(1, 1, 0)$ on the fcc lattice. Here we have defined

$$v_{\nu k}^{F L}(\vec{n} - \vec{n}') = \int dr r^2 \int dr' r'^2 \mathcal{R}_f^2(r) \times v'_{\nu kk'}(\vec{n} - \vec{n}'; r, r') \mathcal{R}_{l_1}(r') \mathcal{R}_{l_2}(r'), \quad (3.30)$$

with $v'_{\nu kk'}(\vec{n} - \vec{n}'; r, r')$ given by Eq. (2.18).

The matrix elements of V'_ν between conduction electron states are treated in analogy with Eqs. (3.15)-(3.19). Now only inter-site terms occur. In the limit $\vec{q} \rightarrow 0$ and \vec{p} close to the star of \vec{p}^X we find

$$U_{QQT}^{cc} = i \sum_{\vec{p}\vec{q}} \sum'_{\nu(k)} v_{\nu k}^{L L'}(\vec{p}, \vec{q}) \eta\left(\rho_k^L(-\vec{p}) \rho_k^{L'}(\vec{p})\right) u_\nu(\vec{q}). \quad (3.31)$$

Here again we have the same relation between the indices ν and k as was the case for Eq. (3.28). The coupling matrix reads

$$v_{\nu 3}^{L L'}(\vec{q}, \vec{p}) = \frac{1}{\sqrt{Nm}} \Lambda^{L L'} q_\nu a \cos\left(\frac{p_x a}{2}\right) \cos\left(\frac{p_y a}{2}\right), \quad (3.32)$$

with $\Lambda^{L L'}$ given by $v_{\nu k}^{L L'}(\vec{n} - \vec{n}')$, with $\nu = x$ or y , for $k = 3$. We finally quote the definition

$$v_{\nu k}^{L L'}(\vec{n} - \vec{n}') = \int dr r^2 \int dr' r'^2 \mathcal{R}_{l_1}(r) \mathcal{R}_{l_2}(r) \times v'_{\nu kk'}(\vec{n} - \vec{n}'; r, r') \mathcal{R}_{l'_1}(r') \mathcal{R}_{l'_2}(r'), \quad (3.33)$$

where we use expression (2.18). Numerical values of $\Lambda^{L L'}$ are given in Table 2.

Taking into account the contributions due to conduction electrons, we see that the interaction Hamiltonian (2.29) has to be replaced by

$$U = U_{TT} + U_{QQ} + U_{QQT}, \quad (3.34)$$

where

$$U_{QQ} = U_{QQ}^{ff} + U_{QQ}^{fc} + U_{QQ}^{cc}, \quad (3.35a)$$

$$U_{QQT} = U_{QQT}^{ff} + U_{QQT}^{fc} + U_{QQT}^{cc}, \quad (3.35b)$$

Before studying the quadrupolar ordering and the accompanying lattice contraction (Sect. V) during the $\gamma \rightarrow \alpha$ phase transition, we will next investigate the crystal field of γ -Ce in the presence of conduction electrons.

IV. CRYSTAL FIELD OF γ -CE

In the disordered γ phase there are only charge density fluctuations of quadrupolar type and the quadrupolar Hamiltonian (3.34) (or (2.29)) averages to zero. The

first nontrivial orientational interaction then corresponds to a crystal field Hamiltonian. In Ref. I we have defined the crystal field of γ -Ce as the potential experienced by a single $4f$ electron at a site \vec{n} when spherically symmetric contributions ($l'=0$) from nuclei, core electronic shells, conduction electrons, $4f$ electrons at the twelve neighboring sites \vec{n}' on the fcc lattice and similar terms from the homogeneous electronic density in the interstitial regions are taken into account. In I we have shown that crystal field effects are reduced to a single particle term to which we have added a spin-orbit coupling for the $4f$ electron. We first generalize the results of I by taking into account the radial dependence of the $4f$ electron density. We start from Eq. (2.8) with $\Lambda = (l = 4, A_{1g}) \equiv \Lambda_1$ and $\Lambda' = (l = 0, A_{1g}) \equiv 0$. Since we are dealing with a Coulomb potential and a spherically symmetric charge distribution, the coupling function $v_{\Lambda_1 0}(\vec{n}, \vec{n}'; r, r')$, Eq. (2.3b), does not depend on r' and we observe that Eq. (2.6) can be written as

$$v_{\Lambda_1 0}^F(\vec{n} - \vec{n}') = v_{\Lambda_1 0}^F \cdot Q_f, \quad (4.1a)$$

where

$$v_{\Lambda_1 0}^F \cdot = \int dr r^2 \mathcal{R}_f^2(r) v_{\Lambda_1 0}(\vec{n}, \vec{n}'; r, r') \quad (4.1b)$$

is the same for all 12 neighbors. We obtain $v_{\Lambda_1 0}^F \cdot < 0$. The charge in units e of the $4f$ electron at a neighboring site is given by

$$Q_f = \int dr' r'^2 \mathcal{R}_f^2(r'). \quad (4.1c)$$

In our model $Q_f = 1$. However, if we distinguish two regions in the crystal, the first inside muffin-tin (MT) spheres and the second in the interstices, then in the MT-region $Q_f < 1$. The other contributions to the crystal field are dealt with similarly. Since the interaction parameter $v_{\Lambda_1 0}^F \cdot$ remains the same it is only the charges Q_i (i stands for core, nucleus, conduction electrons and interstitial contributions) which we shall take care of. Collecting the contributions from the various charges Q_i together with Q_f , we obtain for the crystal field at site \vec{n}

$$V_{CF}^f(\vec{n}) = B^f \rho_{\Lambda_1}^F(\vec{n}), \quad (4.2a)$$

where $\Lambda_1 \equiv (l = 4, A_{1g})$,

$$B^f = \frac{12}{\sqrt{4\pi}} Q_{eff} e v_{\Lambda_1 0}^F \cdot \quad (4.2b)$$

and

$$\rho_{\Lambda_1}^F(\vec{n}) = \sum_{ij} c_{\Lambda_1}^F |i\rangle_{\vec{n}} \langle j|_{\vec{n}}. \quad (4.2c)$$

Here e refers to the electron charge at site \vec{n} ($e = -1$) and Q_{eff} to the effective charge of the surrounding neighborhood. From electrostatic considerations we find (see

Appendix A of I) that $Q_{eff} = (1 + x_{int})Q_{MT}$, where Q_{MT} is the total charge inside a MT-sphere (which is always positive) and where the factor $x_{int} \approx 2.853$ accounts for the charge contributions from interstices for touching MT-spheres. The coefficients $c_{\Lambda_1}^F$, Eq. (4.2c), are quoted in Appendix A of I, they are diagonal in the basis (A.9-A.11) of I. The expressions (4.2a)-(4.2c) represent a refinement of the crystal field calculations, Eqs. (A.3)-(A.6) of I, where now a radial distribution of the $4f$ electron is taken into account.

In I we have calculated the crystal field coefficient B^f (we used the notation Λ for B^f) for a fixed radius r_f . The obtained value $B^f = 346$ K corresponds to $r_f = 1.156$ a.u. and not to $r_f = 1.378$ a.u. as was quoted erroneously in I. With a radial distribution as specified in models 1), 2), and 3) of Sect. II, we obtain $B^f = 970, 1403$ and 1104 K, respectively. This implies that the strength of the crystalline electric field of the $4f$ electron should be 2.8-4 times larger than calculated in Ref. I and therefore by the same factor (2.8-4) larger than the crystal field measured experimentally [23,24]. However, expression (4.2a) is implicitly based on the approximation that the distribution of conduction electrons at site \vec{n} is spherically symmetric and hence the on-site interaction from $l = 4$ multipoles is ignored. In the following we will show that the effective crystal field decreases if we take into account the average on-site cubic distribution ($l = 4$) of conduction electrons.

From Eqs. (3.14a,b) for the on-site interactions we observe that the $4f$ electronic density $\rho_{\Lambda_1}^F$ couples with the conduction electron density of the same symmetry ($\Gamma = A_{1g}, l = 4$). In real space Eq. (3.14a) with $\Lambda = \Lambda' = (l = 4, A_{1g}) \equiv \Lambda_1$ reads

$$U^{fc}|_{intra} = C_{\Lambda_1 \Lambda_1}^F \sum_{\vec{n}} \rho_{\Lambda_1}^F(\vec{n})^\dagger \rho_{\Lambda_1}^L(\vec{n}). \quad (4.3)$$

We obtain the crystal field potential due to $\rho_{\Lambda_1}^L(\vec{n})$, Eq. (3.12a), by replacing this quantity by its thermal average:

$$\langle \rho_{\Lambda_1}^{l_1 l_2} \rangle = \frac{1}{N} \sum_{\vec{k}, \alpha} n_{\vec{k}}^\alpha c_{\Lambda_1 d d}(\vec{k}, \alpha; \vec{k}, \alpha) \delta_{l_1 2} \delta_{l_2 2}. \quad (4.4)$$

Here $n_{\vec{k}}^\alpha \delta_{\vec{q} 0} \delta_{\alpha \beta} = \langle a_{\vec{k} \alpha}^\dagger a_{\vec{k} - \vec{q} \beta} \rangle$ is the Fermi distribution and $l_1 = 2, l_2 = 2$ takes into account the fact that only d electrons contribute to the matrix element $c_{\Lambda_1 l_1 l_2}$. We then write $\langle \rho_{\Lambda_1}^c \rangle = \langle \rho_{\Lambda_1}^{d d} \rangle$. The corresponding crystal field at site \vec{n} reads

$$V_{CF}^{fc}(\vec{n}) = B^{fc} \rho_{\Lambda_1}^F(\vec{n}), \quad (4.5a)$$

where

$$B^{fc} = C_{\Lambda_1 \Lambda_1}^F \langle \rho_{\Lambda_1}^{d d} \rangle, \quad (4.5b)$$

with $C_{\Lambda_1 \Lambda_1}^{F dd} > 0$. Collecting the contributions (4.2a) and (4.5a) we obtain the effective single particle potential acting on the $4f$ electron at site \vec{n} :

$$\tilde{V}_{CF}^f(\vec{n}) = [B^f + B^{fc}] \rho_{\Lambda_1}^f(\vec{n}). \quad (4.6)$$

We recall that $B^f > 0$. The sign of B^{fc} depends on $\langle \rho_{\Lambda_1}^c \rangle$. We next investigate other interactions that affect $\langle \rho_{\Lambda_1}^c \rangle$.

We consider the crystal field acting on $\rho_{\Lambda_1}^c(\vec{n})$. By studying the inter-site interactions we find that the matrix elements $v_{\Lambda\Lambda'}(\vec{n}, \vec{n}'; r, r')$, Eq. (2.3b), are negligibly small for $l = l' = 4$. On the other hand terms with $l = 4, l' = 0$ are significant and we retain the interactions which involve

$$v_{\Lambda_1 0}^{dd \bullet} = \int dr r^2 \mathcal{R}_d^2(r) v_{\Lambda_1 0}(\vec{n}, \vec{n}'; r, r'), \quad (4.7)$$

where $v_{\Lambda_1 0}^{dd \bullet} < 0$ (compare with Eq. (4.1b)). Here again $v_{\Lambda_1 0}^{dd \bullet}$ is independent of r' . Proceeding in analogy with the calculation of V_{CF}^f , we calculate the field due to the surrounding $4f$ electrons, core electrons, nuclei, conduction electrons and interstitial contributions at site \vec{n} , thereby obtaining

$$V_{CF}^c(\vec{n}) = B^c \rho_{\Lambda_1}^c(\vec{n}), \quad (4.8a)$$

where $\rho_{\Lambda_1}^c(\vec{n}) = \rho_{\Lambda_1}^{dd}(\vec{n})$ and

$$B^c = \frac{12}{\sqrt{4\pi}} Q_{eff} e v_{\Lambda_1 0}^{dd \bullet}, \quad (4.8b)$$

with $B^c = 6093 K > 0$. The positive sign of the field B^c implies that $\langle \rho_{\Lambda_1}^c \rangle$, calculated with the crystal field $V_{CF}^c(\vec{n})$, is negative. Hence B^{fc} , Eq. (4.5b), is negative, which leads to a reduction of the effective crystal field of a $4f$ electron in Eq. (4.6).

The previous considerations indicate that the inclusion of conduction electrons leads to a reduction of the crystal field experienced by a $4f$ electron. However, a more rigorous approach should start with the crystal field Hamiltonian of γ -Ce,

$$U_0 = U_0^c + U_{CF} + U_{so}. \quad (4.9)$$

Here U_0^c is the “bare” electronic term (3.6), which includes the kinetic energy and the spherically symmetric part of the electronic potential of conduction electrons, $U_{so} = \sum_{\vec{n}} V_{so}(\vec{n})$ stands for the spin-orbit couplings of localized $4f$ electrons (see Appendix A of I for details). U_{CF} is the crystal field comprising $4f$ electrons and conduction electrons:

$$U_{CF} = \sum_{\vec{n}} V_{CF}(\vec{n}), \quad (4.10a)$$

$$V_{CF}(\vec{n}) = V_{CF}^f(\vec{n}) + V_{CF}^{fc}(\vec{n}) + V_{CF}^c(\vec{n}) + V_{CF}^{cc}(\vec{n}). \quad (4.10b)$$

Here

$$V_{CF}^{cc}(\vec{n}) = C_{\Lambda_1}^{dd dd} \rho_{\Lambda_1}^{dd}(\vec{n})^\dagger \rho_{\Lambda_1}^{dd}(\vec{n}) \quad (4.11)$$

is the on-site $l = 4, l' = 4$ interaction between conduction electrons. In a mean-field approximation U_{CF} leads to self-consistent crystal field potentials $\tilde{V}_{CF}^c(\vec{n})$ and $\tilde{V}_{CF}^f(\vec{n})$ for conduction and $4f$ electrons, respectively. A quantitative calculation of these effects is beyond the scope of the present work.

V. QUADRUPOLEAR ORDERING

In Section III we have found that the system of localized $4f$ electrons and of conduction electrons are coupled by means of the intra-site and inter-site quadrupolar potentials (3.23b) and (3.23a). Such a bilinear coupling suggests that an ordering of $4f$ electron density quadrupoles should imply an ordering of conduction electron quadrupoles and vice versa. In Appendix A we have investigated the wave vector dependence of the quadrupole-quadrupole interaction matrices and the condition for quadrupolar order. The present section is divided into two parts. In part A we study the interplay of quadrupolar ordering of $4f$ electrons and conduction electrons on a rigid cubic lattice; in part B, where we consider a deformable lattice, we show that quadrupolar ordering implies a lattice contraction.

A. We are investigating the possibility of a condensation of quadrupolar densities in a $Pa\bar{3}$ structure. At the X -point of the BZ, the matrices of inter-site interactions $(v_k^F L'_k(\vec{q}))$ and $(v_k^L L'_k(\vec{q}))$ become diagonal in k, k' and have two degenerate negative eigenvalues. We then are led in analogy with the condensation scheme (2.16a,b) for $4f$ electrons to suggest the condensation scheme $Fm\bar{3}m \rightarrow Pa\bar{3}$ for the quadrupole densities of conduction electrons:

$$\bar{\rho}_3^L(\vec{q}_x^X) = \bar{\rho}_1^L(\vec{q}_y^X) = \bar{\rho}_2^L(\vec{q}_z^X) = \bar{\rho}^L \sqrt{N} \neq 0; \quad (5.1a)$$

$$\bar{\rho}_2^L(\vec{q}_x^X) = \bar{\rho}_3^L(\vec{q}_y^X) = \bar{\rho}_1^L(\vec{q}_z^X) = 0, \quad (5.1b)$$

where $L = (sd), (ds), (dd)$.

We disentangle the various contributions to U_{QQ} , Eq. (3.35a), in the ordered α phase where we assume a simultaneous condensation of quadrupolar densities of $4f$ electrons and conduction electrons. Taking into account the condensation scheme (2.16a,b), we obtain from Eq. (2.13)

$$\frac{1}{N} U_{QQ}^{ff} = \frac{3}{2} \lambda^{FF} (\bar{\rho}^F)^2, \quad (5.2)$$

where λ^{FF} stands for $\lambda_{X_5^+}$, the twofold degenerate negative eigenvalue of $v^{FF}(\vec{q}^X)$ (see Appendix A). Similarly, using in addition the condensation scheme (5.1a,b), we obtain from Eq. (3.23b)

$$\frac{1}{N} U_{QQ}^{fc} \Big|_{intra} = 3 [2C^{F ds} \bar{\rho}^F \bar{\rho}^{ds} + C^{F dd} \bar{\rho}^F \bar{\rho}^{dd}], \quad (5.3a)$$

and from Eq. (3.23a)

$$\frac{1}{N} U_{QQ}^{fc} \Big|_{inter} = 3 [2\lambda^{Fds} \bar{\rho}^F \bar{\rho}^{ds} + \lambda^{Fdd} \bar{\rho}^F \bar{\rho}^{dd}], \quad (5.3b)$$

where λ^{Fds} and λ^{Fdd} are the twofold degenerate negative eigenvalues of the matrices $v^{Fds}(\vec{q}^X)$ and $v^{Fdd}(\vec{q}^X)$, respectively (see Appendix A). Finally expressions (3.25b) and (3.25a) lead to

$$\frac{1}{N} U_{QQ}^{cc} \Big|_{intra} = \frac{3}{2} [4C^{sdsd}(\bar{\rho}^{sd})^2 + 4C^{sdd} \bar{\rho}^{sd} \bar{\rho}^{dd} + C^{dddd}(\bar{\rho}^{dd})^2], \quad (5.4a)$$

and

$$\frac{1}{N} U_{QQ}^{cc} \Big|_{inter} = \frac{3}{2} [4\lambda^{sdsd}(\bar{\rho}^{sd})^2 + 4\lambda^{sdd} \bar{\rho}^{sd} \bar{\rho}^{dd} + \lambda^{dddd}(\bar{\rho}^{dd})^2]. \quad (5.4b)$$

We observe that all coefficients $C^{LL'}$ are positive while $\lambda^{LL'}$ are negative (see Table 2). Obviously the inter-site interaction (5.4b) favors quadrupolar order while the intra-site coupling (5.4a) disfavors quadrupolar order of conduction electrons.

The leading quadrupolar interaction in the ordered α phase,

$$U_{QQ} = U_{QQ}^{ff} + U_{QQ}^{fc} \Big|_{intra} + U_{QQ}^{fc} \Big|_{inter} + U_{QQ}^{cc} \Big|_{intra} + U_{QQ}^{cc} \Big|_{inter}, \quad (5.5)$$

is a quadratic form in $\bar{\rho}^F$, $\bar{\rho}^{sd}$ and $\bar{\rho}^{dd}$, in particular the terms (5.3a) and (5.3b) represent a bilinear coupling between the localized $4f$ quadrupolar density $\bar{\rho}^F$ and the conduction electron quadrupolar densities $\bar{\rho}^{dd}$ and $\bar{\rho}^{sd}$. Since in tight-binding the $(6s5d)^3$ electrons are hybridized, we introduce the total conduction electron density

$$\bar{\rho}^c = \bar{\rho}^{dd} + 2\bar{\rho}^{sd}. \quad (5.6)$$

Defining average interaction coefficients

$$C^{fc} = \frac{1}{2}(C^{Fds} + C^{Fdd}), \quad (5.7a)$$

$$\lambda^{fc} = \frac{1}{2}(\lambda^{Fds} + \lambda^{Fdd}), \quad (5.7b)$$

$$C^{cc} = \frac{1}{3}(C^{dsds} + C^{dddd} + C^{dsdd}), \quad (5.7c)$$

$$\lambda^{cc} = \frac{1}{3}(\lambda^{dsds} + \lambda^{dddd} + \lambda^{dsdd}), \quad (5.7d)$$

we approximate U_{QQ} by an effective interaction

$$\frac{1}{N} U_{QQ} \approx \frac{3}{2} [\lambda^{FF}(\bar{\rho}^F)^2 + 2A^{fc} \bar{\rho}^F \bar{\rho}^c + A^{cc}(\bar{\rho}^c)^2], \quad (5.8)$$

where

$$A^{fc} = C^{fc} + \lambda^{fc} \quad (5.9a)$$

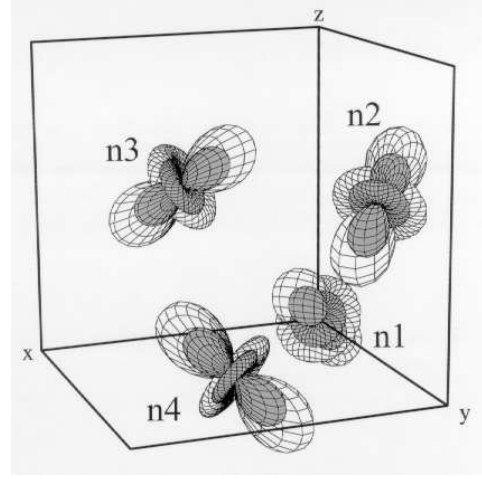


FIG. 3. $Pa\bar{3}$ structure of the ordered α phase with 4 sublattices ($n1 - n4$). Grey quadrupoles correspond to inner $4f$ electron densities, white quadrupoles - to outer conduction electron densities with the opposite sign as shown in figure 4.

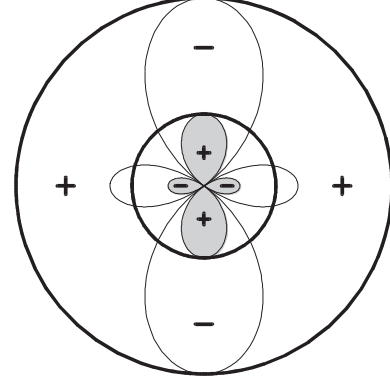


FIG. 4. Quadrupolar density distribution of the $4f$ electron (inside sphere of $r=1.3$ a.u.) and of one conduction electron (spherical radius $r=3.4$ a.u.), on scale.

and

$$A^{cc} = C^{cc} + \lambda^{cc}. \quad (5.9b)$$

We observe that $A^{fc} > 0$, $A^{cc} > 0$. For a fixed value of $\bar{\rho}^F$, we minimize U_{QQ} with respect to $\bar{\rho}^c$ and obtain

$$\bar{\rho}^c = -\frac{A^{fc}}{A^{cc}} \bar{\rho}^F. \quad (5.10)$$

We see that quadrupolar order $\bar{\rho}^F$ of $4f$ electrons produces (as a type of mirror image) a quadrupolar order of conduction electrons $\bar{\rho}^c$ of opposite sign. Herewith we associate the pictorial representation of Fig. 3 and 4. Regions of an excess density (+) of the $4f$ electron distribution overlap with a depletion (-) in density of the conduction electrons and vice versa (Fig. 4). Substituting the right hand side of Eq. (5.10) into (5.8) we get

$$\frac{1}{N}U_{QQ} = -\frac{3}{2} \left[|\lambda^{FF}| + \frac{(A^{fc})^2}{A^{cc}} \right] (\bar{\rho}^F)^2 \quad (5.11)$$

where we use the fact that $\lambda^{FF} < 0$. The bilinear coupling between quadrupolar densities of $4f$ electrons and conduction electrons leads to an increase of the attractive interaction between $4f$ quadrupolar densities.

The results of the last two sections can be summarized by suggesting an effective Hamiltonian in the disordered γ phase,

$$H = U_{QQ} + U_0, \quad (5.12)$$

where U_0 is the crystal field Hamiltonian, (4.9), and

$$U_{QQ} = U_{QQ}^{ff} + U_{QQ}^{fc} + U_{QQ}^{cc}. \quad (5.13)$$

Here

$$U_{QQ}^{ff} = -\frac{1}{2} |\lambda^{ff}| (\rho_2^f(\vec{q}_x^X)^\dagger \rho_2^f(\vec{q}_x^X) + \rho_3^f(\vec{q}_x^X)^\dagger \rho_3^f(\vec{q}_x^X)) + c.p., \quad (5.14a)$$

$$U_{QQ}^{fc} = A^{fc} \sum_{\vec{q}} \sum_k \rho_k^f(\vec{q})^\dagger \rho_k^c(\vec{q}), \quad (5.14b)$$

$$U_{QQ}^{cc} = \frac{1}{2} A^{cc} \sum_{\vec{q}} \sum_k \rho_k^c(\vec{q})^\dagger \rho_k^c(\vec{q}), \quad (5.14c)$$

where $\rho_k^f(\vec{q})$, $k = 1 - 3$, is the quadrupolar density operator (2.10a) of $4f$ electrons while $\rho_k^c(\vec{q})$ is the quadrupolar density of conduction electrons (3.21) with $\rho_k^c = \rho_k^{dd} + 2\rho_k^{sd}$. The first term, Eq. (5.14a), represents an effective attraction at the X point of the Brillouin zone. The other terms in (5.14a) (*c.p.*) follow by cyclic permutation of indices, *i.e.* when $\vec{q}_x^X \rightarrow \vec{q}_y^X$, k changes $2 \rightarrow 3$ and $3 \rightarrow 1$, etc. The direct lattice is face centered cubic. In that case the condensation schemes (2.16a,b) and (5.1a,b) correspond to a structural phase transition where the space group changes from $Fm\bar{3}m$ to $Pa\bar{3}$.

Starting from the interaction (5.8) we construct a Landau free energy in the condensed phase. We take $\bar{\rho}_1 \equiv \bar{\rho}^F$ and $\bar{\rho}_2 \equiv \bar{\rho}^c$ as components of a two dimensional vector $\bar{\rho} = (\bar{\rho}_1, \bar{\rho}_2)$ and define the matrix

$$J = \begin{bmatrix} -|\lambda^{FF}| & A^{fc} \\ A^{fc} & A^{cc} \end{bmatrix}. \quad (5.15)$$

Inspired from the theory of orientational order in molecular crystals we write

$$\frac{\mathcal{F}}{N} = \frac{\mathcal{F}_0}{N} + \frac{3}{2} \sum_{ij} \bar{\rho}_i \chi_{ij}^{-1} \bar{\rho}_j + \mathcal{F}^{(3)} + \mathcal{F}^{(4)}. \quad (5.16)$$

Here \mathcal{F}_0 is the free energy in the disordered phase:

$$\mathcal{F}_0 = -T \ln \text{Tr}[e^{-U_0/T}], \quad (5.17)$$

where U_0 is the crystal field, Eq. (4.9). The quantity

$$\chi^{-1} = [T \langle \rho \rho \rangle_0^{-1} + J] \quad (5.18)$$

is the inverse susceptibility matrix, T is the temperature and

$$\langle \rho \rho \rangle_0 = \begin{bmatrix} \langle (\rho_k^F(\vec{n}))^2 \rangle_0 & 0 \\ 0 & \langle (\rho_k^c(\vec{n}))^2 \rangle_0 \end{bmatrix}. \quad (5.19)$$

Here $\langle \dots \rangle_0$ are single particle thermal expectation values that have to be calculated by means of U_0 , Eq. (4.9). Cubic symmetry implies (see Appendix B for details) that the three quadrupolar components are equal and for expectation values of conduction electrons we obtain:

$$\langle \rho_k^L(\vec{n}) \rho_{k'}^{L'}(\vec{n}) \rangle_0 = \frac{1}{N^2} \sum_{\alpha \beta} \sum_{\vec{p} \vec{h}} (1 - n_{\vec{p} \beta}) n_{\vec{h} \alpha} \times \left| c_{kL}(\vec{h}, \alpha; \vec{p}, \beta) \right|^2 \delta_{LL'} \delta_{kk'}. \quad (5.20)$$

Here $\delta_{LL'} = \delta_{l_1 l_1'} \delta_{l_2 l_2'}$. The contributions $\mathcal{F}^{(3)}$ and $\mathcal{F}^{(4)}$ stand for the third and fourth order terms in $\bar{\rho}$. Symmetry of the order parameter components (see condensation schemes (2.16a,b) and (5.1a,b)) implies that there exists a non-zero third order cubic invariant $\mathcal{F}^{(3)}$ and hence the transition $Fm\bar{3}m \rightarrow Pa\bar{3}$ is of first order. As a first approximation we investigate the possibility of a second order phase transition. Neglecting $\mathcal{F}^{(3)}$ and $\mathcal{F}^{(4)}$, we minimize \mathcal{F} with respect to $\bar{\rho}^F$ and to $\bar{\rho}^c$. We obtain two coupled homogeneous equations from which it follows again that $\bar{\rho}^F$ and $\bar{\rho}^c$ have to be of opposite sign. The compatibility condition leads to the transition temperature

$$T_C = \frac{1}{2} \left(J_{ff} - J_{cc} + \sqrt{(J_{ff} + J_{cc})^2 + 4(J_{fc})^2} \right), \quad (5.21)$$

where

$$J_{ff} = |\lambda^{FF}| \langle (\rho_k^F(\vec{n}))^2 \rangle_0, \quad J_{cc} = A^{cc} \langle (\rho_k^c(\vec{n}))^2 \rangle_0, \quad (5.22a)$$

$$J_{fc} = A^{fc} \sqrt{\langle (\rho_k^F(\vec{n}))^2 \rangle_0 \langle (\rho_k^c(\vec{n}))^2 \rangle_0}. \quad (5.22b)$$

We observe that $T_C > J_{ff}$ and the inclusion of conduction electrons leads to an increase of transition temperature. The calculation of the first order transition temperature T_1 , ($T_1 > T_C$), and of the accompanying discontinuities $\bar{\rho}^c(T_1)$ and $\bar{\rho}^F(T_1)$ in the coupled order parameters would require the evaluation of the higher order terms $\mathcal{F}^{(3)}$ and $\mathcal{F}^{(4)}$. Such an endeavor poses not only analytical but also numerical problems that are beyond the scope of the present work. We therefore will adopt below (Sect. 6) an alternative point of view and suggest experiments in order to check qualitatively the predictions of the theory.

B. We next investigate the lattice strains at the transition to the $Pa\bar{3}$ phase. We recall the result U_{QQT}^{ff} ,

Eq. (2.27), for the coupling of strains to $4f$ electrons with quadrupolar order. The same procedure, as outlined in Sect. 2, is now applied to derive the coupling of longitudinal strains to conduction electrons. Using the condensation schemes (2.16a,b) and (5.1a,b) and taking into account the definitions of interaction parameters Λ (Table 2), we obtain from Eqs. (3.28) and (3.29)

$$\frac{1}{N}U_{QQT}^{fc} = -4a \left[2\Lambda^{Fds} \bar{\rho}^F \bar{\rho}^{ds} + \Lambda^{Fdd} \bar{\rho}^F \bar{\rho}^{dd} \right] \sum_{\nu} \epsilon_{\nu\nu}. \quad (5.23)$$

Similarly we get from from Eqs. (3.31) and (3.32)

$$\begin{aligned} \frac{1}{N}U_{QQT}^{cc} = & -2a \left[4\Lambda^{dsds} (\bar{\rho}^{ds})^2 + 4\Lambda^{dsdd} \bar{\rho}^{ds} \bar{\rho}^{dd} \right. \\ & \left. + \Lambda^{dddd} (\bar{\rho}^{dd})^2 \right] \sum_{\nu} \epsilon_{\nu\nu}. \end{aligned} \quad (5.24)$$

The coefficients Λ are quoted in Table 2. We define the total interaction potential of ordered quadrupolar electron densities coupled to longitudinal strains by

$$U_{QQT} = U_{QQT}^{ff} + U_{QQT}^{fc} + U_{QQT}^{cc}. \quad (5.25)$$

Here the right hand side terms are given by Eqs. (2.27), (5.23) and (5.24), respectively. In analogy with expressions (5.7b,d) we define

$$\Lambda^{fc} = \frac{1}{2}(\Lambda^{Fds} + \Lambda^{Fdd}), \quad (5.26a)$$

$$\Lambda^{cc} = \frac{1}{3}(\Lambda^{dsds} + \Lambda^{dddd} + \Lambda^{dsdd}), \quad (5.26b)$$

and use again definition (5.6). Then we approximate U_{QQT}/N by an effective interaction

$$\begin{aligned} \frac{1}{N}U_{QQT} \approx & -2a[\Lambda^{FF}(\bar{\rho}^F)^2 + 2\Lambda^{fc}\bar{\rho}^F\bar{\rho}^c + \Lambda^{cc}(\bar{\rho}^c)^2] \\ & \times \sum_{\nu} \epsilon_{\nu\nu}. \end{aligned} \quad (5.27)$$

This relation allows us to express the longitudinal strains as function of the order parameters. The contributions U_{TT} and U_{QQT} lead to a supplementary term in the free energy (compare with Eq. (5.16)):

$$\frac{1}{N}\mathcal{F}_{QQT} = \frac{1}{N}U_{TT} + \frac{1}{N}U_{QQT}. \quad (5.28)$$

(There are still additional contributions from thermal lattice vibrations, but these are irrelevant here.) For a given quadrupolar order, *i.e.* $\bar{\rho}^F$ and $\bar{\rho}^c$ fixed, we minimize $\mathcal{F}_{QQT}[\bar{\rho}^F, \bar{\rho}^c, \epsilon_{\nu\nu}]$ with respect to the strains ϵ_{xx} , ϵ_{yy} and ϵ_{zz} and obtain

$$\begin{aligned} \epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz} = & 8a^{-2}\kappa_L \\ & \times [\Lambda^{FF}(\bar{\rho}^F)^2 + 2\Lambda^{fc}\bar{\rho}^F\bar{\rho}^c + \Lambda^{cc}(\bar{\rho}^c)^2], \end{aligned} \quad (5.29)$$

where a is the cubic lattice constant and where κ_L is the bare linear compressibility. From the numerical values of Table 2 we obtain $\Lambda^{FF} = -498$, $\Lambda^{fc} = -1205$, $\Lambda^{cc} = -2966$ (units K/Å). Since $\bar{\rho}^F$ and $\bar{\rho}^c$ are of opposite sign, the fc contribution on the right hand side of expression (5.29) leads to an expansion of the lattice while the ff and cc contributions lead to a contraction. From Table 2 we also find that $A^{fc} = 30516$ K, $A^{cc} = 24033$ K, and hence from Eq. (5.10) we deduce that $|\bar{\rho}^c| > |\bar{\rho}^F|$. Hence we conclude that inclusion of the conduction electrons in expression (5.29) leads to an increase of the lattice contraction by a factor 4.4 in comparison with the effect of the $4f$ electrons. A numerical calculation of the lattice contraction $\Delta a = a\epsilon_{xx}$ at the first order phase transition would require the knowledge of the discontinuities $\bar{\rho}^c(T_1)$ and $\bar{\rho}^F(T_1)$. Experimentally [1] one finds in the pressure (P) - temperature phase diagram of the $\gamma - \alpha$ transition in Ce indications of a critical end point where the lattice contraction vanishes. Although the transition $Fm\bar{3}m \rightarrow Pa\bar{3}$ is always of first order and hence leads to finite discontinuities of $\bar{\rho}^c(T_1)$ and $\bar{\rho}^F(T_1)$, there exists the possibility that the relative importance of the coefficients Λ^{fc} and Λ^{cc} , which have opposite sign, changes as a function of (P, T) and hence the expression within square brackets on the right hand side of Eq. (5.29) could vanish or even change sign without the requirement that $\bar{\rho}^c(T_1) = 0$ and $\bar{\rho}^F(T_1) = 0$. This opens up a possibility of a lattice expansion during the discussed first order phase transition. Recent experiments on YbInCu₄ which exhibits an isostructural phase transition similar to the $\gamma - \alpha$ change observed in cerium (see [20] for references) indicate a 0.5% volume expansion at the transition. Within the present theory such behavior can be understood if for Yb in YbInCu₄ the fc term responsible for expansion prevails over ff and cc contributions, Eq. (5.29).

VI. DISCUSSION

The present paper is an extension of our previous model of the $\gamma - \alpha$ phase transition in Ce (Ref. [21] or I). We predict that the $\gamma - \alpha$ transition is accompanied by a symmetry change $Fm\bar{3}m \rightarrow Pa\bar{3}$ in the electronic structure. The idea of such a proposal is borrowed from the theory of molecular crystals, where $Pa\bar{3}$ structures due to orientational order of molecular mass distribution are not unusual. For example, such crystal symmetry occurs in NaO₂ [29], N₂ [30] and in solid C₆₀ [31]. The conventional characterization of the $\gamma - \alpha$ transition in Ce as a phase transition “without change of symmetry” is based on several X-ray diffraction experiments [1]. It is possible that domain formation in the α -phase has precluded an identification of this phase as a $Pa\bar{3}$ structure. If new experiments are done, particular attention should be given to the possible coexistence of domains [32].

In comparison with our previous work, Ref. I, we have extended the model in two respects. First, we have included quadrupolar interactions between $4f$ and conduction electrons and secondly, we have calculated the relevant parameters of interactions (Table 2 and Sect. 2) by using the radial dependences of valence electrons obtained from a DFT-LDA calculation of a cerium atom. To our knowledge, in the literature there exists no microscopic derivation of multipolar interactions between conduction and localized electrons in solids although the concept of quadrupolar moment of a $4f$ electron shell is well established [33,34]. Therefore in Sect. 3 we have presented a detailed calculation of multipolar interactions treating band conduction electrons in second quantization with wave functions in tight-binding approximation. Since the intersite quadrupole-quadrupole interaction is short ranged and anisotropic, special attention has been given to lattice site symmetry. While we have restricted ourselves here (see in particular Appendix A) to the case of an fcc lattice ($\gamma \rightarrow \alpha$ Ce), our procedure is general and can easily be extended to other structures.

Our results can be understood on the basis of the following generalized Hamiltonian which we ascribe to the γ phase:

$$H_\gamma = U_0 + U_{QQ} + U_{QQT} + U_{TT}. \quad (6.1)$$

Here U_0 is the crystal field Hamiltonian (4.9). The term U_{QQ} represents the quadrupole-quadrupole interaction comprising contributions from $4f$ and conduction electrons (Eq. (3.35a)). The quadrupolar interaction between localized electrons is due only to intersite contributions on the fcc lattice, see Eq. (2.13) in Fourier space. The presence of conduction electrons leads to two types of contributions: inter-site terms, given by (3.23a) and (3.25a) for U_{QQ}^{fc} and U_{QQ}^{cc} , respectively, and on-site terms, given by (3.23b) and (3.25b), correspondingly. Collecting inter-site and on-site terms separately, we write

$$U_{QQ} = U_{QQ}|_{inter} + U_{QQ}|_{intra}, \quad (6.2)$$

where

$$U_{QQ}|_{inter} = \sum_{\vec{q}} \sum_{k,k'} \left(\frac{1}{2} v_k^F F_{k'}(\vec{q}) \rho_k^F(\vec{q})^\dagger \rho_{k'}^F(\vec{q}) + v_k^F L_{k'}(\vec{q}) \rho_k^F(\vec{q})^\dagger \rho_{k'}^L(\vec{q}) + \frac{1}{2} v_k^L L_{k'}(\vec{q}) \eta \left(\rho_k^L(\vec{q})^\dagger \rho_{k'}^L(\vec{q}) \right) \right), \quad (6.3a)$$

and the summation over $L(L') = (sd), (ds), (dd)$ is implied. The structure of the interaction matrices $v^{AB}(\vec{q})$, $A(B) = F$ or L , is discussed in Appendix A, the relevant eigenvalues λ^{AB} at \vec{q}^X are quoted in Table 2. The intra-site contributions are given by

$$U_{QQ}|_{intra} = \sum_{\vec{q}} \sum_k (C^{FL} \rho_k^F(\vec{q})^\dagger \rho_k^L(\vec{q}))$$

$$+ \frac{1}{2} C^{LL'} \eta \left(\rho_k^L(\vec{q})^\dagger \rho_k^{L'}(\vec{q}) \right), \quad (6.3b)$$

where the calculated parameters C^{AB} are quoted in Table 2. Next in Eq. (6.1), U_{QQT} , given by (3.35b), is a correction to U_{QQ} for a deformable lattice, while U_{TT} is the elastic energy of the cubic crystal in harmonic approximation. In terms of homogeneous strains, U_{TT} is given by Eq. (2.28) and U_{QQT} by Eq. (5.25). In principle a bilinear coupling term U_{QT} between quadrupolar electronic and displacive degrees of freedom [35] should be included in expression (7.1). This term which is known from Jahn-Teller phase transitions [36] can be essential if we want to describe transitions from a cubic phase with quadrupolar disorder to non cubic phases with ferro-quadrupolar order [37]. However for the transition to the $Pa\bar{3}$ phase, which we identify with α -Ce, the atomic center of mass positions still occupy a face centered cubic lattice and the term U_{QT} is irrelevant. Indeed, the driving force for the transition $Fm\bar{3}m \rightarrow Pa\bar{3}$ is the quadrupole-quadrupole interaction which becomes attractive (in reciprocal space) at the X point of the Brillouin zone. This fact leads to an orientational order of quadrupolar electronic densities on four different sublattices (Figs. 3, 4). The term U_{QQT} then prompts a lattice contraction at the first order phase transition. Notice that the term U_{QT} is found to vanish for a wave vector \vec{q} at the X point of the BZ. We insist on these facts since within our view, the electronic charge degrees of freedom, together with the lattice displacements, are the driving forces of structural phase transitions in Ce and related compounds.

The Hamiltonian (7.1) is not sufficient to describe the magnetic phenomena that occur at the $\gamma - \alpha$ transition [12,1]. In accordance with Kramers' theorem the quadrupolar ordering, as described by Eq. (7.1) is not accompanied by a magnetic ordering. We then conclude that the addition of an Anderson Hamiltonian term H_{cf} which takes into account the Friedel-Anderson hybridization between conduction electrons and $4f$ electrons as well as the repulsive energy among the $4f$ electrons on a same site is necessary (for a review see [38]). Such a Hamiltonian leads to the disappearance of local magnetic moments below a characteristic temperature T_K . The Kondo temperature T_K increases with increasing hybridization matrix element V . We then conclude that the lattice contraction accompanying the $Pa\bar{3}$ quadrupolar ordering or the quadrupolar order enhances the hybridization V and hence increases T_K . This can lead to a situation where the structural $\gamma \rightarrow \alpha$ transition and the demagnetization of the $4f$ state occur at a same temperature T_1 . Notice however that within this scenario the process is driven by the structural (quadrupolar) transition at T_1 and not by the Kondo volume collapse [8,9]. In case where the enhancement of T_K is insufficient, the quadrupolar order and the concomitant lattice contraction would occur at T_1 without Kondo anomaly (disap-

pearance of magnetic moment). The condition $T_K < T_1$ does not ensure that the Kondo anomaly actually occurs at lower T . Quadrupolar ordering has been observed in a number of Ce, Pr, Tm and U based compounds [33]. A remarkable example is the magnetic semiconductor TmTe with $4f^{13}$ ($^2F_{7/2}$) electronic configuration and Néel temperature $T_N=0.43$ K [39]. Although TmTe had been extensively studied before 1995, the phenomenon of quadrupole ordering below $T_Q=1.8$ K was completely overlooked [40,41]. Numerous data on such compounds (CeAg [34], CeB₆ [42], TmTe [40], TmAu₂ [43], DyB₂C₂ [44] etc.) with quadrupole phase transitions show that the magnetic ordering occurs at lower T . A transition to an ordered magnetic phase in these rare-earth intermetallic compounds indicates that the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction between localized magnetic moments prevails over the Kondo transition mechanism (for a review, see [45]). In zero magnetic field the magnetic susceptibility shows no anomaly at T_Q for TmTe [40], CeAg [34] and a very small anomaly for DyB₂C₂ [44], TmAu₂ [43]. Within the present work we come to the conclusion that quadrupolar order, as an electronic charge degrees of freedom driven process on one hand, and magnetic properties (Kondo anomaly, magnetic order) on the other hand are related indirectly via their coupling to lattice displacements. An open question is a possible relation between quadrupolar order and hybridization. In our opinion a microscopic derivation of the Anderson hybridization Hamiltonian which should include details about the symmetry of the lattice site and the electronic orbitals constitutes a challenge for further work.

ACKNOWLEDGMENTS

We thank B. Lengeler, V.V. Moshchalkov, K. Parlin-ski, R.M. Pick and H. Wagner for helpful criticism and discussions. We are grateful to J.L. Sarrao and Z. Fisk for drawing our attention to YbInCu₄. A.V.N. thanks J.-M. Mignot and I.V. Solovyev for useful remarks. This work has been financially supported by the Fonds voor Wetenschappelijk Onderzoek, Vlaanderen.

VII. ERRATUM FOR REFERENCE [21]

In Table 3 $-\beta$ (last column, third row) should be replaced with $+\beta$. In the last column of Table 5 $-\lambda$ (first row) should be replaced with $+\lambda$, $-\mu$ (second row) - with ν and $-\nu$ (third row) - with μ . In Table 2 $i = 7, 8$ correspond to $\Gamma_7, 2$ (third row, second column) while $i = 13, 14$ - to Γ_6 (fifth row, second column). In equation (4.7d) $c_3^{(2)}(hl) c_4^{(2)}(li)$ has to be replaced by $c_2^{(2)}(il) c_2^{(2)}(li)$, on the right hand side of equation (5.11) in front of summation it should stay i , not $\frac{i}{2}$.

APPENDIX A:

The Fourier transforms of the intersite electronic quadrupole-quadrupole interactions are 3×3 matrices where the rows and columns are labeled by the indices of the T_{2g} functions S_2^k , $k = 1, 2, 3$. The structure of these matrices depends on the symmetry of the lattice and of the T_{2g} functions. The magnitude of the elements depends on the nature of the electrons (localized $4f$, or conduction $6s$, $5d$) and we abbreviate the electronic indices f or s , d by the label A, B for $F = (ff)$ or $L = (l_1 l_2)$ writing $v_{k k'}^{AB}$ for $v_{k k'}^{ffsd}$ etc.. We consider elements

$$v_{k k'}^{AB}(\vec{q}) = \sum_{\vec{h} \neq 0} v_{k k'}^{AB}(\vec{h}) e^{i\vec{q} \cdot \vec{X}(\vec{h})}. \quad (A1)$$

Here $v_{k k'}^{AB}(\vec{h})$ refers to the elements in real space with $\vec{h} = \vec{n}' - \vec{n}$. Taking the site \vec{n} as origin on a fcc lattice, the index \vec{n}' (or \vec{h}) labels the twelve neighbors. Compare with expressions (2.6), (3.10a) and (3.17) for the case $\Lambda = (T_{2g}, k)$, $\Lambda' = (T_{2g}, k')$. Performing the lattice sums and using the symmetries of the elements $v_{k k'}^{AB}(\vec{h})$ we obtain

$$v^{AB}(\vec{q}) = 4 \begin{bmatrix} \gamma^{AB} C_{yz} + \alpha^{AB} (C_{zx} + C_{xy}) & -\beta^{AB} S_{xy} & -\beta^{AB} S_{zx} \\ -\beta^{AB} S_{xy} & \gamma^{AB} C_{zx} + \alpha^{AB} (C_{xy} + C_{yz}) & -\beta^{AB} S_{yz} \\ -\beta^{AB} S_{zx} & -\beta^{AB} S_{yz} & \gamma^{AB} C_{xy} + \alpha^{AB} (C_{yz} + C_{zx}) \end{bmatrix} \quad (A2)$$

where $C_{ij} = \cos(q_i a/2) \cos(q_j a/2)$, and $S_{ij} = \sin(q_i a/2) \times \sin(q_j a/2)$. Here i, j stands for the Cartesian indices x, y, z , and a is the cubic lattice constant. Additional information on coupling matrices can be found in Ref. [47] where a problem with similar symmetries was considered for a molecular crystal. The quantities γ^{AB} , α^{AB} and β^{AB} stand for the matrix elements $v_{k k'}^{AB}(\vec{h})$ for $\vec{h} = a(1/2, 1/2, 0)$ with $(k = 3, k' = 3)$, $(k = 1, k' = 1)$ and $(k = 1, k' = 2)$, respectively. The interaction matrix $v^{AB}(\vec{q})$ has the largest negative twofold degenerate eigenvalue at the X -point of the Brillouin zone. For instance for $q_x^X = (2\pi/a)(1, 0, 0)$ $\lambda_{X_5^+}^{AB} = -4\gamma^{AB}$, where $\gamma^{AB} = v_{33}^{AB}(\vec{h}) = v_{22}^{AB}(\vec{h}) > 0$. Hence the quadrupolar interaction parameters $\lambda_{X_5^+}^{AB}$ are completely specified, their numerical values are given in Table 2, fourth column.

APPENDIX B:

We study the symmetry properties of the Bloch functions and rewrite Eq. (3.1) as

$$\begin{aligned} \langle \vec{R} | \vec{k}, \alpha \rangle &= \psi_{\vec{k}, \alpha}(\vec{R}) \\ &= \frac{1}{\sqrt{N}} \sum_{\vec{n}'} e^{i\vec{k} \cdot \vec{X}(\vec{n}')} \sum_{l\tau} \gamma_{l\tau}(\vec{k}, \alpha) \phi_{l\tau}(\vec{R} - \vec{X}(\vec{n}')). \end{aligned} \quad (B1)$$

Here $\phi_{l\tau}(\vec{r}) = \mathcal{R}_l(\vec{r})S_l^\tau(\Omega)$ where $S_l^\tau(\Omega)$ are basis functions of the irreducible representations of O_h . Here again $\tau \equiv (\Gamma, \mu, k)$. We recall that

$$Y_l^m(\Omega) = \sum_{\tau} \beta_l^{m\tau} S_l^\tau(\Omega), \quad (\text{B2a})$$

where β_l is a unitary matrix. It follows that

$$\gamma_{l\tau}(\vec{k}, \alpha) = \sum_m \gamma_{lm}(\vec{k}, \alpha) \beta_l^{m\tau} \quad (\text{B2b})$$

We observe that the expression (3.10b) becomes

$$\begin{aligned} & c_{k'l_1l_2}(\vec{k}, \alpha; \vec{p}, \beta) \\ &= \sum_{\tau_1 \tau_2} \gamma_{l_1\tau_1}^*(\vec{k}, \alpha) \gamma_{l_2\tau_2}(\vec{p}, \beta) c_{k'}(l_1\tau_1, l_2\tau_2), \end{aligned} \quad (\text{B3a})$$

where

$$c_{k'}(l_1\tau_1, l_2\tau_2) = \int d\Omega S_{l_1}^{\tau_1}(\Omega) S_{k'}(\Omega) S_{l_2}^{\tau_2}(\Omega). \quad (\text{B3b})$$

The Bloch functions can be rewritten as basis functions of a d -dimensional irreducible representation of the space group $Fm\bar{3}m$ which is induced by a small representation $\Gamma_{\vec{k}_1}^{(p)}$ of the little group of a chosen wave vector \vec{k}_1 . Here p labels the small representation. One has $d = q \cdot t$, where q is the number of arms of the star of \vec{k}_1 : $^*\vec{k}_1 = \{\vec{k}_1 \dots \vec{k}_i \dots \vec{k}_q\}$, and where t is the dimension of the small representation. (If \vec{k}_1 is not a high symmetry vector of the Brillouin zone, $q = 48$, the order of the group O_h , $t = 1$ and $d = 48$.) The basis functions $\langle \vec{R} | \vec{k}_i, s_p, \alpha \rangle$, where $s_p = 1 - t$ and $\vec{k}_i \in ^*\vec{k}_1$, all have the same energy. We can use the small representation index p to label the energies. Hence we will write for the band index α the composite index (p, ν) , where ν labels the small representations p that occur more than once. We consider (see also Appendix B of Ref. I)

$$\begin{aligned} \sum_{s_p=1}^t \sum_{i=1}^q |\langle \vec{R} | \vec{k}_i, s_p, \alpha \rangle|^2 &= \frac{1}{N} \sum_{\vec{n}'} \phi_{l\tau}^*(\vec{r}_{\vec{n}'}) \phi_{l'\tau'}(\vec{r}_{\vec{n}'}) \\ &\times \sum_{s_p=1}^t \sum_{i=1}^q \gamma_{l\tau}^*(\vec{k}_i, s_p, \alpha) \gamma_{l'\tau'}(\vec{k}_i, s_p, \alpha) \end{aligned} \quad (\text{B4})$$

for fixed p and $\vec{k}_i \in ^*\vec{k}_1$. By the generalized Unsöld theorem [49] this expression is an invariant of $Fm\bar{3}m$ for any $\vec{r}_{\vec{n}'}$. This means that the site symmetry is O_h and the density $\sum_k \phi_{l(\Gamma\mu k)}^*(\vec{r}_{\vec{n}'}) \phi_{l(\Gamma\mu k)}(\vec{r}_{\vec{n}'})$ stays invariant for any representation Γ and index μ of O_h (Unsöld theorem). We therefore obtain the condition

$$\begin{aligned} & \sum_{s_p=1}^t \sum_{i=1}^q \gamma_{l\tau}^*(\vec{k}_i, s_p, \alpha) \gamma_{l'\tau'}(\vec{k}_i, s_p, \alpha) \\ &= \delta_{ll'} \delta_{\tau\tau'} f[\vec{k}_1 \alpha; \Gamma, \mu], \end{aligned} \quad (\text{B5})$$

where \vec{k}_1 belongs to a basis domain Φ [25] and where f is a function of \vec{k}_1 and depends on the labels Γ, μ, α .

Now we calculate the single particle expectation values $\langle (\rho_k^{l_1l_2}(\vec{n}))^2 \rangle_0$, Eq. (5.20), for conduction electrons. From Eqs. (3.12a,b) we have

$$\begin{aligned} \langle \rho_k^{l_1l_2}(\vec{n}) \rho_{k'}^{l'_1l'_2}(\vec{n}) \rangle_0 &= \frac{1}{N} \sum_{\vec{q}} \langle \rho_k^{l_1l_2}(\vec{q})^\dagger \rho_{k'}^{l'_1l'_2}(\vec{q}) \rangle_0 \\ &= \frac{1}{N^2} \sum_{\vec{q}} \sum_{\vec{p}} \sum_{\vec{h}} \langle a_{\vec{p}-\vec{q}\alpha}^\dagger a_{\vec{p}\beta} a_{\vec{h}+\vec{q}\alpha'}^\dagger a_{\vec{h}\beta'} \rangle_0 \\ &\times c_{k'l_1l_2}^*(\vec{p}, \beta; \vec{p}-\vec{q}, \alpha) c_{k'l'_1l'_2}(\vec{h}+\vec{q}, \alpha'; \vec{h}, \beta'). \end{aligned} \quad (\text{B6})$$

Here summation is understood over the repeated band indices $\alpha, \alpha', \beta, \beta'$. The thermal expectation value is calculated with the single electron Hamiltonian U_0^c , Eq. (3.6). We use standard Green's function (GF) techniques [50] and evaluate first the susceptibility (retarded GF) in the static frequency limit ($z=0$)

$$\begin{aligned} \chi(z=0) &= -\langle \langle a_{\vec{p}-\vec{q}\alpha}^\dagger a_{\vec{p}\beta}; a_{\vec{h}+\vec{q}\alpha'}^\dagger a_{\vec{h}\beta'} \rangle \rangle_{z=0} \\ &= -\frac{n_{\vec{p}-\vec{q}\alpha} - n_{\vec{p}\beta}}{E(\vec{p}-\vec{q}, \alpha) - E(\vec{p}, \beta)} \delta_{\vec{p}-\vec{q}\vec{h}} \delta_{\alpha\beta'} \delta_{\beta\alpha'}. \end{aligned} \quad (\text{B7})$$

Here $n_{\vec{p}\alpha}$ is the Fermi distribution function. Therefrom we get the identity

$$\begin{aligned} n_{\vec{p}-\vec{q}\alpha} - n_{\vec{p}\beta} &= (1 - n_{\vec{p}\beta}) n_{\vec{p}-\vec{q}\alpha} \\ &\times \left[1 - e^{(E(\vec{p}-\vec{q}, \alpha) - E(\vec{p}, \beta))/T} \right]. \end{aligned} \quad (\text{B8})$$

We observe that in the high temperature case the static GF $\langle \langle A; B \rangle \rangle_{z=0}$ is related to the thermal expectation value $\langle AB \rangle$ by

$$\langle AB \rangle_0 = -T \langle \langle A; B \rangle \rangle_{z=0}. \quad (\text{B9})$$

Hence, for $|E(\vec{p}-\vec{q}, \alpha) - E(\vec{p}, \beta)| < T$, we obtain

$$\begin{aligned} \langle \rho_k^{l_1l_2}(\vec{n}) \rho_{k'}^{l'_1l'_2}(\vec{n}) \rangle_0 &= \frac{1}{N^2} \sum_{\alpha\beta} \sum_{\vec{p}\vec{q}} (1 - n_{\vec{p}\beta}) n_{\vec{p}-\vec{q}\alpha} \\ &\times c_{k'l_1l_2}^*(\vec{p}, \beta; \vec{p}-\vec{q}, \alpha) c_{k'l'_1l'_2}(\vec{p}, \beta; \vec{p}-\vec{q}, \alpha). \end{aligned} \quad (\text{B10})$$

We next show that symmetry implies that $k = k'$ and $l_1 = l'_1$, $l_2 = l'_2$. Expression (B10) then reduces to (5.20). We rewrite expression (B10) as

$$\begin{aligned} \langle \rho_k^{l_1l_2}(\vec{n}) \rho_{k'}^{l'_1l'_2}(\vec{n}) \rangle_0 &= \frac{1}{N^2} \sum_{\alpha\beta} \sum_{\vec{p}\vec{h}} (1 - n_{\vec{p}\beta}) n_{\vec{h}\alpha} \\ &\times c_{k'l_1l_2}^*(\vec{p}, \beta; \vec{h}, \alpha) c_{k'l'_1l'_2}(\vec{p}, \beta; \vec{h}, \alpha). \end{aligned} \quad (\text{B11})$$

Using Eq. (B5), we now exploit the fact that the summation over the Brillouin zone can be decomposed by distinguishing the summation over the basic domain from the summation over the components of irreducible representations. Expression (B11) can be rewritten as

$$\langle \rho_k^{l_1 l_2}(\vec{n}) \rho_k^{l'_1 l'_2}(\vec{n}) \rangle_0 = \langle (\rho_k^{l_1 l_2}(\vec{n}))^2 \rangle_0 \delta_{l_1 l'_1} \delta_{l_2 l'_2} \delta_{k k'}, \quad (\text{B12})$$

where

$$\begin{aligned} \langle (\rho_k^{l_1 l_2}(\vec{n}))^2 \rangle_0 &= \sum_{\alpha \beta} \sum_{\vec{h}_1 \in \Phi} \sum_{\vec{p}_1 \in \Phi} \sum_{s_h} \sum_i \sum_{s_p} \sum_j \\ &\left| c_{k l_1 l_2}(\vec{h}_i, s_h, \alpha; \vec{p}_j, s_p, \beta) \right|^2 P(\vec{h}_1 \alpha; \vec{p}_1 \beta). \end{aligned} \quad (\text{B13})$$

Here we have taken into account the property (B5). The quantity P is a function of temperature due to the presence of the Fermi distribution. We next show that expression (B13) is independent of the index of the quadrupolar component k (*i.e.* has the same value for $k=1,2,3$.) We consider the summation over the components of a pair of irreducible representations:

$$\begin{aligned} X &= P(\vec{h}_1 \alpha; \vec{p}_1 \beta) \\ &\times \sum_{s_h} \sum_i \sum_{s_p} \sum_j \left| c_{k l_1 l_2}(\vec{h}_i, s_h, \alpha; \vec{p}_j, s_p, \beta) \right|^2. \end{aligned} \quad (\text{B14})$$

Inserting the explicit expression for $c_{k l_1 l_2}$ we obtain

$$\begin{aligned} X &= \sum_{\Gamma_1 \Gamma_2} \sum_{\mu_1 \mu_2} P'(\vec{h}_1, \alpha, \Gamma_1, \mu_1; \vec{p}_1, \beta, \Gamma_2, \mu_2) \\ &\times \sum_{s_1 s_2} [c_k^*(l_1 \tau_1; l_2 \tau_2)]^2, \end{aligned} \quad (\text{B15})$$

where $\tau_i = (\Gamma_i, \mu_i, s_i)$, $i = 1, 2$. We have used relations (B3a,b) and (B5). The quantity P' is defined by

$$\begin{aligned} P'(\vec{h}_1, \alpha, \Gamma_1, \mu_1; \vec{p}_1, \beta, \Gamma_2, \mu_2) \\ = P(\vec{h}_1 \alpha; \vec{p}_1 \beta) f[\vec{h}_1 \alpha; \Gamma_1, \mu_1] f[\vec{p}_1 \beta; \Gamma_2, \mu_2]. \end{aligned} \quad (\text{B16})$$

Finally we observe that as a consequence of the Wigner-Eckart theorem

$$\sum_{s_1 s_2} c_k^*(l_1 \tau_1; l_2 \tau_2) c_{k'}(l_1 \tau_1; l_2 \tau_2) = \delta_{k k'} \mathcal{C}(\Gamma_1 \mu_1; \Gamma_2 \mu_2), \quad (\text{B17})$$

where \mathcal{C} is independent of k (as a square of a reduced matrix element). This proves that X and correspondingly $\langle (\rho_k^{l_1 l_2}(\vec{n}))^2 \rangle_0$ is independent of k . Finally we quote a property of $\gamma_{l\tau}$ that follows from the completeness of the basis functions

$$\sum_{\alpha} \sum_{\vec{k}_1 \in \Phi} \sum_{s_p=1}^t \sum_{i=1}^q \gamma_{l\tau}^*(\vec{k}_i, s_p, \alpha) \gamma_{l'\tau'}(\vec{k}_i, s_p, \alpha) = \delta_{l l'} \delta_{\tau \tau'} N. \quad (\text{B18})$$

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